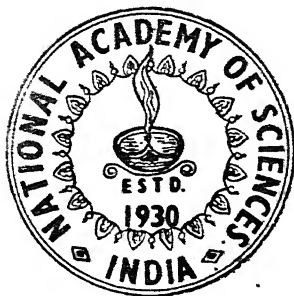


PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1962

Vol. XXXII

SECTION - A

Part II



NATIONAL ACADEMY OF SCIENCES, INDIA
ALLAHABAD

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OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1962

VOL. XXXII

SECTION - A

PART II

STUDY OF THE COMPONENT ACIDS FROM THE VISCERAL
FAT OF THE FISH LABEO ROHITA WITH DIFFERENT
STAGES OF GROWTH

By

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[Received on 23rd November, 1961]

Changes in the chemical composition of the fish fat with different habitat and climate have been reported.¹ Lovern² has reported the variation in the chemical composition of the fat obtained from the same fish during different parts of the year with reference to Herring oil. Black and others³ have studied the variations in the fatty acid composition with the growth of the fish pilchard (*Sardina ocellata*). Fats obtained from the different parts of the same fish have different fatty acid composition.⁴ Fatty acid composition of the fish fat varies in mature as well as in embryonic stages as has been shown in the study of the liver fats from the mature and the embryonic sharks.⁵

In the present paper a detailed study of the component acids of the visceral fat obtained from the different stages of growth of the fish *Labro rohita* has been reported. The following points have been kept in view in connection with the collection of the material.

- (1) The fishes were collected from the same environment.
- (2) They were collected during the same period of the year, which for the purpose of the present work was the last fortnight of June (every year).

(3) A constant change in weight was the main guiding factor in the collection of the material for different stages.

Although the studies on the age and growth of the fishes have been reported in a large number of cases from foreign countries,⁶ in India such a type of study has been done only in the case of *Mrigala* (Ham.) and a few other species.⁷

As the fish *Labeo rohita* has not been studied from this point of view, the age of the fish could not be approximated with regard to the furcal length, breadth and weight. Under these circumstances, the variation of weight by a constant factor (in this case near about 500 gms.) was the only possible criteria of classification into different stages.

The average length, breadth and weight for different stages are shown below :

TABLE I

Measurements	Stage No.					
	1	2	3	4	5	6
Length (cms) ...	28.2	35.9	41.3	51.2	53.4	56.6
Breadth (cms) ...	19.5	23.1	26.3	30.0	33.0	35.4
Weight (gms) ...	500.1	1044.0	1564.0	2024.0	2483.0	2908.0

EXPERIMENTAL

Fish was cut length wise on its ventral side. Viscera was removed from the fish and the liver was removed from the visceral part. The liver-removed visceral portion and the liver were kept separately in acetone. The viscera was extracted two to three times with acetone and the acetone extracts mixed, from which the solvent was distilled off and the residual mass taken up in petroleum ether (b.p. 40-60°) whereby oil dissolved in it. The tissue extracted with acetone was exhaustively extracted with pet. ether (40-60°) and the extracts mixed with the previous one. This was dried by means of anhydrous sodium sulphate and filtered. Solvent was removed completely from the filtrate under reduced pressure and the fat so obtained was kept under vacuum.

The analytical characteristics (*viz.*, Acid value, Sap. value, Iodine value, Hehner value etc.) of the fats were determined by the usual standard methods.

Fat was saponified and the fatty acids were recovered from the soap solution on decomposition with a 10% sulphuric acid solution and subsequent extraction with ether. The fatty acids were resolved into three main groups A, B and C by the joint application of Lithium salt - acetone method⁸ followed by the Hilditch's modification of the Twitchell's⁹ Lead salt-ethanol process.

Acids of each main group were converted into their methyl esters and subsequently fractionated under reduced pressure. Iodine value and saponification value determinations were made on each fraction of the three main groups. The mean unsaturation expressed by the fractional number of hydrogen atoms short of

saturation was determined as usual by interpolation and extrapolation from the respective ester fractions in each group from which the mean of the equivalents of the homologous ester groups (C_{14} , C_{16} , C_{18} , C_{20} , C_{22}) follows.

Analytical characteristics of the visceral fats from the different stages of the fish *Labeo rohita* are given in Table No. II.

TABLE II
Analytical characteristics of the visceral fats from the six stages of the fish *Labeo rohita*

Analytical Charac- teristics		Stage No.					
		1	2	3	4	5	6
% fat	...	20.3	20.8	19.33	22.5	24.69	24.08
Iodine value	...	101.4	96.7	96.38	98.21	102.6	104.8
Saponification value		196.8	204.6	195.3	183.5	181.8	182.5
Hehner value	...	88.37	88.4	87.9	90.7	91.5	91.68
Acid value	...	2.69	2.76	2.78	2.55	2.61	2.80

TABLE III
Analytical characteristics of the mixed acids from visceral fats from the six stages of the fish *Labeo rohita*

Analytical charac- teristics.		Stage No.					
		1	2	3	4	5	6
1. Sap. value	...	203.4	208.9	199.4	186.1	187.1	189.8
2. Iodine value	...	109.6	107.9	104.6	106.9	109.7	112.7

TABLE IV
Analytical characteristics of the acids separated into main groups
(viz. A, B and C)

Stage No.	A			B			C		
	Wt. %	N.V.	I.V.	Wt. %	N.V.	I.V.	Wt. %	N.V.	I.V.
1	25.3	281.4	210.1	27.4	279.1	134.4	47.3	272.8	26.7
2	28.7	278.3	206.4	28.1	273.4	116.7	43.2	274.6	21.6
3	25.8	287.4	204.7	31.4	283.1	122.4	42.8	272.7	22.6
4	25.4	280.3	217.4	28.3	282.1	119.7	46.3	277.8	29.6
5	24.3	289.4	213.9	27.6	276.4	129.9	48.1	263.7	25.6
6	21.4	288.0	229.4	27.7	274.3	124.0	50.9	266.1	20.8

A detailed account of the data of fractionation of methyl esters (and their calculated composition) of the three main groups of acids from the mixed acids of the visceral fat of the fish *Labeo rohita* of stage No. 1 are given in Tables V, VI, VII and VIII. Similarly the data for the visceral fats of the remaining five stages were tabulated but to economise space, only %w/W of the component acids (excluding NSM) of the visceral facts of the six stages are given in Table IX for comparison.

TABLE V

Fractionation of methyl esters of lithium salt - acetone soluble group (A) and calculated composition of ester fractions

Fr. No.	Wt.	S.E.	I.V.	UNSATURATED					NSM
				C ₁₄	C ₁₆	C ₁₈	C ₂₀	C ₂₂	
1	2.97	274.7	154.3	...	2.05	0.92
2	4.78	276.9	162.7	...	2.88	1.90
3	6.27	283.1	170.5	...	2.31	3.96
4	8.19	294.1	181.7	7.95	0.24
5	5.16	301.4	204.5	3.45	1.71
6	4.66	304.3	216.6	2.57	2.09
7	6.77	309.4	230.5	2.39	4.38
8	3.63	314.5	238.7	0.58	3.05
9	1.92	332.0*	300.6	1.23	0.67	0.02
44.35 Wts				...	7.24	23.72	12.70	0.67	0.02
% esters				...	16.32	53.48	28.64	1.51	0.05
% acids				...	16.23	53.42	28.78	1.52	0.05
% in mixed acids				...	4.11	13.52	7.28	0.38	0.01

Unsaturated esters taken as :—

	S.E.	I.V.
C ₁₆	267.0	142.7
C ₁₈	293.4	199.1
C ₂₀	318.9	282.5
C ₂₂	345.3	320.0

TABLE VI
Fractionation of methyl esters of lead salt - ethanol soluble group (B) and
calculated composition of ester fractions

Fr. No.	Wt.	S.E.	I.V.	SATURATED		UNSATURATED			NSM
				C ₁₆	C ₁₈	C ₁₆	C ₁₈	C ₂₀	
1	3.41	271.3	94.7	0.21	Tr.	2.77	0.43
2	5.65	274.1	98.6	0.35	0.06	3.97	1.27
3	6.60	282.4	107.5	0.40	0.35	2.56	3.29
4	3.40	288.9	123.4	0.07	0.16	0.64	2.53
5	4.61	294.4	138.5	0.01	0.09	0.04	4.47
6	4.72	301.4	147.2	3.45	1.27	...
7	3.82	310.6	163.1	1.46	2.36	...
8	2.17	321.4*	174.1	0.30	1.84	0.03
<hr/>									
	34.38	Wts.	...	1.04	0.66	9.98	17.20	5.47	0.03
		% esters	...	3.03	1.92	29.02	50.02	15.92	0.09
		% acids	...	3.02	1.92	28.90	50.06	16.00	0.09
		% in mixed acids	...	0.83	0.53	7.92	13.72	4.38	0.02

Unsaturated esters taken as :—

	S.E.	I.V.
C ₁₆	268.0	94.8
C ₁₈	294.7	142.2
C ₂₀	321.2	189.8

TABLE VII
Fractionation of methyl esters of lead salt-ethanol insoluble group (C) and
calculated composition of ester fractions

Fr. No.	Wt.	S.E.	I.V.	SATURATED				UNSATURATED				INSM
				C ₁₄	C ₁₆	C ₁₈	C ₂₀	C ₁₄	C ₁₆	C ₁₈	C ₂₀	
1	2.17	265.7	10.87	0.27	1.65	0.02	0.23
2	2.19	272.8	15.74	...	1.62	0.20	0.30	0.07
3	3.54	274.6	19.30	...	2.30	0.50	0.55	0.19
4	2.82	280.7	22.80	...	1.25	0.86	0.37	0.34
5	2.64	287.5	24.70	...	0.67	1.23	0.21	0.53
6	5.14	291.7	27.30	...	0.73	2.79	0.23	1.39
7	3.17	295.4	29.40	...	0.18	1.91	0.02	1.06
8	0.97	319.7*	35.60	0.25	0.29	0.16	0.25	0.02
<hr/>												
22.64	Wts.	0.27	8.40	7.74	0.29	0.02	1.91	3.74	0.25	0.02
	% esters	1.19	37.11	34.18	1.28	0.09	8.44	16.52	1.10	0.09
	% acids	1.18	37.01	34.29	1.28	0.08	8.42	16.55	1.10	0.09
	% in mixed acids	0.56	17.51	16.22	0.60	0.04	3.98	7.83	0.52	0.04

All unsaturated esters taken as mono ethenoids.

*Equivalents of esters freed from NSM A₉ = 324.3 ; B₈ = 317.2 ; C₈ = 312.5

TABLE VIII
Visceral Fat : Stage No. 1

Component acids				Sum	Acids w/W	excl. NSM Moles
Acids	A	B	C	(%)	(%)	(%)
Myristic	0.56	0.56	0.56	0.67
Palmitic	...	0.83	17.51	18.34	18.35	19.68
Stearic	...	0.53	16.22	16.75	16.76	16.19
Arachidic	0.60	0.60	0.60	0.52
Unsaturated fractions						
C ₁₄	0.04	0.04	0.04	0.05
C ₁₆	4.11	7.92	3.98	16.01	16.02	17.31
C ₁₈	13.52	13.72	7.83	35.07	35.10	34.34
C ₂₀	7.28	4.38	0.52	12.18	12.19	10.93
C ₂₂	0.38	0.38	0.38	0.31
NSM	0.01	0.02	0.04	0.07
Mean unsaturation of :						
C ₁₄	-2.0	-2.0		
C ₁₆	-3.0	-2.0	-2.0	-2.1		
C ₁₈	-4.6	-3.3	-2.0	-3.5		
C ₂₀	-7.1	-4.8	-2.0	-6.1		
C ₂₂	-8.7	-8.7		

TABLE IX
Component acids excluding the non-saponifiable matter (% w/W)

Acids	1	2	3	4	5	6
Myristic	... 0.56	0.18	0.41	0.70	4.74	3.72
Palmitic	... 18.35	17.30	19.92	19.72	23.68	26.11
Stearic	... 16.76	17.30	15.30	13.27	6.61	13.36
Arachidic	... 0.60	0.70	1.38	2.15	2.01	0.82
Unsaturated fractions						
C ₁₄	... 0.04	1.32	0.01	0.07	0.79	0.61
C ₁₆	... 16.02	24.78	9.79	13.36	19.05	16.93
C ₁₈	... 35.10	29.51	36.19	30.10	30.25	23.74
C ₂₀	... 12.19	8.29	14.68	18.95	10.76	9.54
C ₂₂	... 0.38	0.62	2.32	1.68	2.11	5.17

DISCUSSION

The fatty acid composition of the visceral fats of the fish *Labeo rohita* shows resemblance with the fats of aquatic origin¹⁰, in that the fats contain C_{16} , C_{18} and C_{20} as the major and C_{14} and C_{22} as the minor unsaturated acids. The proportion of C_{22} unsaturated acids usually increases at the later stages in the case of visceral fats.

The major component saturated acids in the fats of aquatic origin is palmitic (10 to 18%) while myristic and stearic acids are present in minor proportions¹⁰ (1 to 2%). In the visceral fats of this fish the percentage of palmitic is markedly higher (17 — 26%). A significant difference is in the high percentage (6 to 17%) of stearic acid. Arachidic acid though a minor component is inevitable and has been reported in a number of Indian fresh water fishes.¹² The distinctive features of the fresh water fish fats are the small proportions of unsaturated C_{20} acids, the predominance of unsaturated C_{18} and C_{16} acids. Although the small proportions of C_{22} unsaturated and predominance of unsaturated C_{18} acids (23-36%) are maintained in the present case, the unsaturated C_{20} acids are not present in reduced proportions (9-18%).

A comparison of the component fatty acids of the fats from the sea water life and the fresh water life reveals significant differences in that the fats of aquatic animals, large or small, differ typically in the proportions of certain component acids according to whether the habitat of the animals is salt or fresh water. In the marine fats C_{16} and C_{18} unsaturated acids are less than those from the fresh water fats while C_{20} and C_{22} are comparatively more in the marine fats. The acids from the visceral fats of the fish *Labeo rohita* shows a similarity with the fats of marine mammalia such as Whale oil¹³, in the increased content of C_{18} unsaturated acids. The percentages of C_{16} and C_{20} unsaturated acids are almost comparable. The C_{22} unsaturated acids are however, in traces ; in all cases less than 2.32% except in the last stage where it occurs to the extent of 5.17%.

The analysis and examination of the visceral fat of the six stages reveals that there is an increase in the saponification value by 8 units from the first to second stage and then there is a gradual drop in the subsequent stages, clearly showing that in the beginning the lower acids are being formed up to the second stage and then the higher ones in the subsequent stages. This fact is further confirmed by the analysis of the component acids which clearly shows that C_{18} and C_{20} unsaturated acids decrease in the second stage and then increase in the third stage. The percentage of C_{22} unsaturated acids progressively increases from the first to the sixth stage.

Amongst the saturated acids there is gradual increase in the proportions of arachidic acid up to the fourth stage and then slight decrease in the fifth and sixth stages. The proportions of stearic acid show a steady decrease up to the fifth stage and then a sudden increase in the sixth stage. In the sixth stage, stearic acid increases considerably with the corresponding decrease in the amount of arachidic acid. The variations of palmitic and myristic acids are not very marked but it will be noticed that the proportions of palmitic acid vary from 17 to 26%.

The mean unsaturation of the acids from the visceral fats of the fish *Labeo rohita* presents another interesting study. The mean unsaturation of C_{16} acids present in the fish fats is mostly -2.2 except in few cases where it is to the extent of -2.6 to -3.5. The mean unsaturation of C_{18} acids ranges from -2.5 to -4.0 though in the case of Herring (*Glupea harengus*) body fat, it is reported to be -4.0 to

-10.0. The body fat of herring has C_{22} acids with mean unsaturation between -4.0 to -5.0, while the study of other fish fats either of the fresh water or salt water reveals that they are more unsaturated (-6.5 to -10.0).

The observations on the mean unsaturation of the acids obtained from the visceral fats of the six different stages of the fish *Labeo rohita*, besides being within the limits of the range as observed for those from other fishes is also more or less (except in one or two stages) in agreement with the observations of Pathal *et al.* The mean unsaturation of C_{18} , C_{20} and C_{22} acids shows general agreement but that of C_{16} acids is slightly lower in practically all the cases.

ACKNOWLEDGEMENT

One of us (K. C. S.) wishes to express his grateful thanks to the Council of Scientific and Industrial Research, Govt. of India for the award of a Junior Research Assistantship in a scheme on the subject.

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11. Pathak S. P. and Agarwala C. V. : *Biochem. J.*, 51, 264 (1952) ; Pathak S. P., Pande G. D. and Mathur S. S. : *Biochem J.*, 57, 447 (1954).
12. Hilditch : *The Chemical Constitution of Natural Fats* 1956 Edn., page 64, Table 20.

SEMIMICRO DETERMINATION OF NITRO GROUP BY REDUCTION WITH STANNOUS CHLORIDE

By

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[Received on 18th November, 1961]

ABSTRACT

A semimicro procedure for the determination of nitro groups by reduction with stannous chloride has been described. 20-25 mg of the samples were reduced by refluxing in an inert atmosphere for 3 hours at 100°C with 25 ml of 0.5 N stannous chloride. After reduction the contents were made up to 250 ml and 50 ml of this were titrated in presence of nitrogen against 0.1 N iodine solution using an automatic burette. A magnetic stirrer was used for stirring the solution in the course of titration. To avoid nuclear chlorination excess of chloride ions were reduced by dissolving stannous chloride in least amount of hydrochloric acid. Necessary hydrogen ions for reduction and subsequent titration were provided by the addition of 2-3 ml (1:1 by volume) of sulphuric acid in each determination. In most cases glacial acetic acid was used as solvent for dissolving the samples. Aldehyde free ethanol was used as solvent for the steam volatile samples or for those insoluble in glacial acetic acid.

A blank was run with each determination.

The formation of amino compounds by the reduction of nitro groups is frequently employed as a method for the determination of the nitro groups present in an organic compound. The amino compound can be titrated directly or more frequently, the excess of the reducing agent being estimated by back titration. As early as 1878 stannous chloride was used as a reducing agent.¹ Since then several modifications of the original method have been proposed by various investigators.^{2,3,4,5,6,7}

The nitro compound is usually reduced by heating in an inert atmosphere with excess of the reducing agent dissolved in hydrochloric acid. The solution is cooled and the excess of stannous chloride titrated back against iodine or ferric chloride using starch and ammonium thiocyanate respectively as indicator.

The stannous chloride reduction has been shown to give low results with many substances. Nuclear chlorination by excess of chloride ions present, has been put forward as a possible explanation for this^{8,9,10} and it has been suggested to reduce the amount of chloride ions by replacing the excess of hydrochloric acid by sulphuric acid as a source of hydrogen ions necessary for the process of reduction and subsequent titration of the excess reducing agent against iodine or ferric chloride.

The above procedure, with all its modifications and using the best possible ideal conditions has been employed in the present work in order to determine the percentage of nitro groups, employing 20-25 mg samples. Although, as already mentioned above, sulphuric acid has been recommended as an alternative source of hydrogen ions in order to reduce the excess of chloride ions, it has also been found that a large excess of sulphuric acid lowers the rate of reduction. Hence an excess of sulphuric acid also should be avoided and it is necessary to strike a mean between the two.

The strength of stannous chloride (2.5 N to 3 N) used for reduction in the macro scale has been brought down to 0.5 N in the semimicro scale, though few substances like 3:5 dinitrobenzoic acid and *m*-nitrobenzoic acid could be reduced even with 0.05 N stannous chloride.

TABLE I
Showing the percentage of nitro group using 0.5 N stannous chloride as reducing agent.

Nitro compounds	Percentage of nitro group			
	Calculated	Found		
3:5 Dinitrobenzoic acid*	43.39	43.05	43.17	42.93
<i>p</i> -Nitrobenzoic acid	27.54	27.10	27.16	27.08
4-Chloro, 1:3-dinitro benzene	45.45	45.39	45.27	45.19
Nitrobenzene	37.40	37.20	37.23	37.21
<i>m</i> -Nitrobenzoic acid*	27.54	27.34	27.40	27.22
<i>o</i> -Nitrobenzaldehyde	30.46	29.77	30.12	29.95

EXPERIMENTAL

(i) **Reagents :**

- (a) *Stannous chloride solution* : A 0.5 N stannous chloride solution was prepared by dissolving A. R. (B. D. H.) stannous chloride in the least quantity of M. A. R. (H. and W.) concentrated hydrochloric acid. Amount of hydrochloric acid should in no case be in excess. It was diluted to the requisite strength with freshly boiled distilled water and cooled in presence of nitrogen. An atmosphere of nitrogen was maintained over the solution.
- (b) *Iodine solution* : A stock solution of 0.1 N iodine was prepared by dissolving A. R. (B. D. H.) iodine in potassium iodide in water and diluting with distilled water.
- (c) *Potassium Iodide* : M. A. R. grade (Hopkins and Williams Ltd., London).
- (d) *Sodium Thiosulphate solution* : (A. R., B. D. H.) A 0.1 N solution was prepared and standardised against standard copper sulphate solution.
- (e) *Starch* : (A. R., B. D. H.) A 1.0% solution of starch was prepared afresh each day.
- (f) *Alcohol* : A rapid stream of nitrogen was passed during several hours through the alcohol heated under reflux condenser, to make it aldehyde free.

* Using 0.05N stannous chloride.

(g) *Glacial Acetic Acid* : Glacial acetic acid (B. D. H., A. R.) was used.

(h) *Sulphuric acid* : M. A. R. grade (H. and W.)

(ii) Procedure :

20-25 mg. of the pure and dry sample was weighed in a pyrex glass shell vial and the vial along with the sample was carefully transferred to a Jena glass 150 ml. conical flask, which had an arrangement for passing nitrogen gas and had a B₁₉ ground joint to affix the B₁₉ condenser. The sample was dissolved in distilled water, dilute hydrochloric acid (A. R.) or glacial acetic acid (A. R.) which ever could dissolve it. In a few cases, small amounts (2 ml.) of dilute sulphuric acid (M. A. R.) can be used as the solvent if the sample is found to be soluble in it and insoluble in other solvents mentioned above. However, glacial acetic acid dissolved most of the samples which were insoluble in water or dilute hydrochloric acid. Ethanol was used as a solvent only when the sample was either insoluble in any of the solvents mentioned above or was volatile with steam. The use of ethanol should, however, be avoided as far as possible. Sometimes a little warming was necessary to dissolve the sample in the solvent. It has been found that even if the sample was insoluble in any of the above solvents, it slowly dissolved in the reducing agent during the course of the reaction as the temperature gradually rose.

A slow stream of nitrogen gas (one to two bubbles per second) was passed through the flask for five minutes to remove air from the flask completely. 2-3 ml. of sulphuric acid (1:1 by volume) and 25 ml. of stannous chloride were then added and the contents of the flask were swirled slowly for one minute to make them homogenous. An efficient water condenser was affixed to the flask and the flask heated on a water bath or on a controlled electric mantle and the temperature allowed to rise slowly to 100°C. (If the sample is not volatile with steam and alcohol is not being used, an air condenser can be used in place of water condenser). The reduction required about three hours for completion. Nitrobenzene required more drastic conditions for reduction and the reduction was complete only after heating for four to four and half hours. In the case of volatile compounds, after about one and half hours of heating the sides of the condenser were rinsed with 5 ml. of ethanol to dissolve and bring back any volatilised portion of the compound to the reaction flask.

After the reduction was complete, the flask was rapidly cooled, passing nitrogen gas during the entire operation. The contents of the flask were carefully transferred to a 250 ml. Jena flask inside which the air had been replaced by nitrogen. The reaction flask was rinsed four times with 10 ml. portions of air free distilled water and washings transferred to the same measuring flask ; the entire operation of transferring the contents and rinsing the reaction flask was completed within a time period of one to one and half minutes. The contents were rapidly made up to the mark with air-free distilled water. 50 ml. of this solution were carefully transferred to a 150 ml. Jena flask from which air had previously been replaced by passing nitrogen gas for two minutes. Nitrogen was allowed to bubble at the rate of one to two bubbles per second. The solution was stirred continuously using a magnetic stirrer and titrated against 0.1 N iodine solution from an automatic micro-burette. Freshly prepared 1% solution of starch was used as indicator. A hundred watt, single coiled, day light lamp, clamped at a height of one foot over the titration vessel was used to illuminate the flask in order to judge the change in colour at the end point in a better way.

A blank was run maintaining the identical conditions and using all the reagents except the sample during the entire procedure of reduction. The transference of the

contents to the measuring flask in the case of blank must take the same time and rinsing should be done the same number of times with 10 ml. portions of distilled water. From the difference between the two readings (blank and actual) iodine equivalent to the stannous chloride used up in the reduction of the sample was calculated. Separate blanks were run for each set of determinations.

ACKNOWLEDGEMENT

One of the authors (J. P. S.) thanks the Ministry of Education, Government of India, for the award of a S. R. T. Scholarship.

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ON THE APPLICABILITY OF CUPROUS-CUPRIC AND COPPER AMALGAM ELECTRODES FOR THE STUDY OF THE BIURET REACTION

By

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[Received on 12th January, 1962]

ABSTRACT

The biuret reaction of hydrolysed casein, and biuret and those of glycine and leucine with Cu^{++} ions was studied at the cuprous-cupric and copper-amalgam electrode. The results indicate that the biuret combines with Cu^{++} ion in equimolecular proportions while hydrolysate of casein two molecules or free amino acids combine with one copper. The latter ratio was also found to exist in biuret complexes of glycine and leucine with the help of copper-amalgam electrode.

Electrometric methods have found little use in studying the biuret reaction of amino acids and proteins. In our earlier communication, we have shown that polarographic and amperometric methods could be successfully employed in determining the composition of biuret¹, malonamide², serine³, asparagine⁴ and cyanuric acid⁵. However, on applying these methods to the biuret reaction of proteins⁶, precise information regarding the binding of copper to nitrogen could not be obtained and the ratio copper to nitrogen varied from 1:2.2 to 1:5.4. Besides, the potentiometric method (employing the cuprous-cupric electrode) gave still less satisfactory results and only in a few cases was the upper limit (1.5.4), found by amperometry, realised. Since factors like adsorption of interacting ions by proteins and the non-equilibrium condition at the electrode might be responsible for the discrepancies, it was thought worthwhile to carry out investigations, with simpler molecules, as already done in the case of polarographic studies (*loc-cit*).

This communication deals with the reactions of Cu (II) with biuret and hydrolysed casein using the cuprous-cupric electrode. Results on the potentiometry of copper-glycine and copper nor-leucine complexes at the amalgam electrode are also incorporated here.

EXPERIMENTAL

Biuret was prepared by the method recommended by Haworth and Mann.⁷ 0.1M solution was prepared by dissolving the requisite amount in doubly distilled water. Potentiometric titrations were carried out with the following solutions: (i) 2.5 cc. 0.1M biuret + 10 cc. buffer (pH, 12.04) + 1 cc. 0.01M Cu_2Cl_2 , (ii) 3.0 cc. 0.1M biuret + 9.5 cc. buffer (pH 12.04) + 1 cc. 0.01M Cu_2Cl_2 , (iii) 4 cc. 0.1M biuret + 13 cc. 1.0M KOH + 1 cc. 0.01M Cu_2Cl_2 , (iv) 5 cc. biuret 0.1M + 12 cc. 1.0M KOH + 1 cc. 0.01M Cu_2Cl_2 , (v) 6 cc. biuret 0.1M + 11 cc. 1.0M KOH + 1 cc. 0.01M Cu_2Cl_2 . A bright platinum electrode dipped in these mixtures served as the indicator electrode. Measurements were carried out with the help of a Fisher S type potentiometer. 0.1M CuSO_4 was used as the titrant (Typical curve shown in Fig. 1).

The casein hydrolysate was prepared as follows: 5 gms of casein (E. Merck) was taken in a round bottomed flask and to it was added 25 cc of 8M H_2SO_4 . The mixture was refluxed over an oil bath for about twenty-four hours to provide the standard for complete hydrolysis.⁸ The mixture was then cooled, diluted and sulphuric acid removed as barium sulphate. Filtrate and washings were treated

with animal charcoal to yield a clear solution (pH 5.0 to 5.5). The hydrolysate was made upto 400cc. and kept in a refrigerator. Titrations were carried out

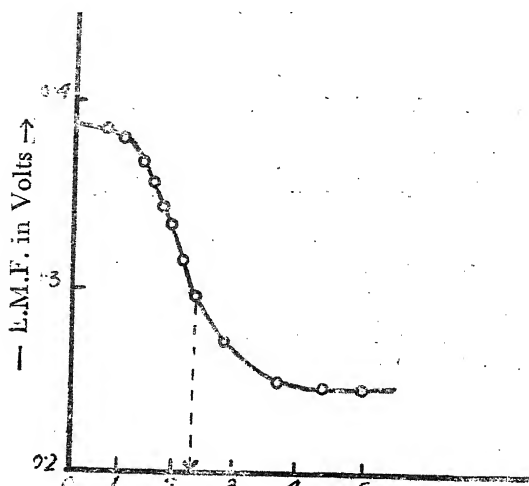


Fig. 1

— Vol. of 0.1M CuSO₄ in cc →
4cc 0.1M Biuret + 13cc. 1.0M KOH + 1cc.
0.01M Cu₂Cl₂ in the titration_{cell}

with 10cc. of 0.02M CuSO₄ solution containing 0.2cc, 0.5 cc and 1.0cc 0.01M Cu₂Cl₂ respectively. 5cc. of the hydrolysate in 20cc buffer of pH 8.7 was used as the titrant (typical curve shown in Fig. 2). Copper amalgam was

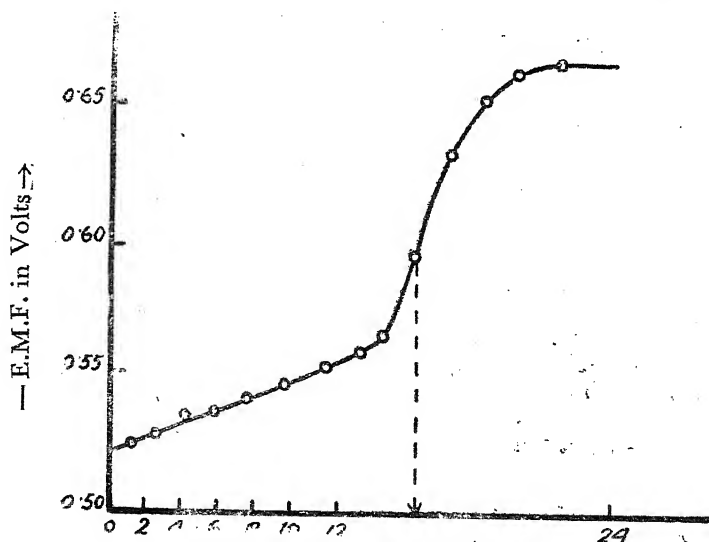


Fig. 2

— Vol. of Hydrolysate (pH 8.7) in cc →
10cc 0.02M CuSO₄ + 0.5cc 0.01M Cu₂Cl₂ in the cell

prepared by the electrolysis of 0.5M acidified copper sulphate solution, using a current of about 5 amp. per sq. decimeter of mercury and a copper anode⁹.

Solutions of glycine and nor-leucine (B.D.H.) were prepared by dissolving the requisite amount of the acids in doubly distilled water and the titrations with the following sets were carried out : (i) 5 cc 0.02M glycine + 10 cc buffer (pH 8.7), (ii) 5 cc 0.01M glycine + 10 cc buffer (pH 8.7), both titrated against 0.01M copper sulphate ; (iii) 5 cc 0.02M nor-leucine + 5 cc buffer (pH 8.7) titrated against 0.02M copper sulphate (Typical curves shown in Fig. 3).

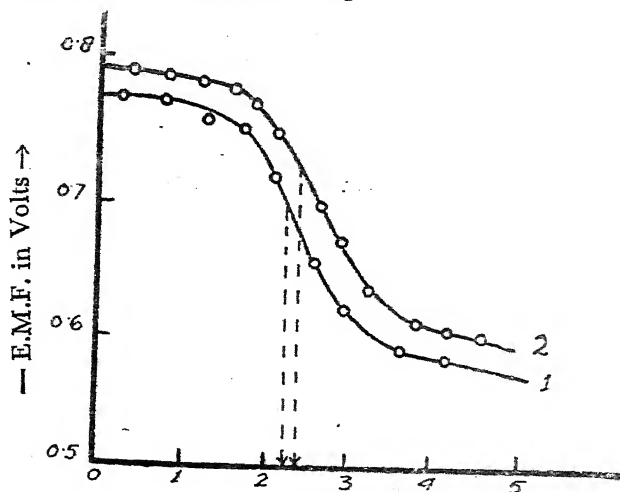
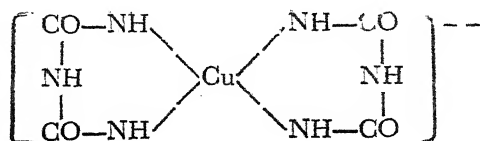


Fig. 3
— Vol. of 0.02M CuSO_4 in cc →
Curve 1. 5cc 0.02M Glycine + 10cc Buffer pH 8.7
Curve 2. 5cc 0.02M Nor-Leucine + 5cc Buffer pH 8.7

RESULTS AND DISCUSSION

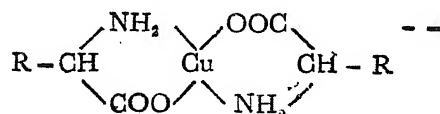
Potentiometric titrations at the cuprous-cupric electrode give typical curves in the alkaline medium (0.1M KOH). Since excess of alkali is present in the medium, the cupric ions after the completion of the reaction remain in solution in the form of cuprate ions, thereby allowing a large shift in the potential (due to the presence of Cu already present) near the end point. The combining ratio comes out to 2:1 (Biuret : copper) and the structure of the complex can be represented as



and confirm the results of other workers. However, on carrying out the titration in the buffer of pH 12.04, sharp breaks are not realised. On the other hand, the potential becomes constant after the addition of a certain amount of copper sulphate solution (this is quite possible in view of the low solubility of copper phos-

phate in comparison to copper sulphate). If the end point is taken where the potential becomes constant, the combining ratio comes out to be 1:1 confirming the results of our earlier investigations.¹

In the case of the interaction of the hydrolysates of casein with cupric ions a sharp jump in potential is realised even in presence of 5×10^{-4} M cuprous ions. From the end point it was found that two nitrogen atoms are bound per atom of copper, if the concentration of the hydrolysate can be represented in term of the total nitrogen present in the protein (14.0% for casein, determined by Kjeldahl's method using micro-distillation assembly). The ratio appears to be correct since the hydrolysate consists of only free amino acids and two molecules of amino acid would combine with one copper to form the complex of the general structure.



Incidentally the method can be employed for the estimation of nitrogen in proteins provided the product is taken in the hydrolysed form.

The e. m. f. of copper amalgam electrode at any concentration of Cu is given by $E = E_0 - 0.059 \log \text{Cu}$ where E_0 is the standard potential of copper-cupric system. Titrations carried out at this indicator electrode provide a sharp break at the end point, showing a binding of 2 molecules of amino acid (either glycine or nor-leucine) with one atom of copper. The complex formed can be represented in a manner similar to that for casein hydrolysate. Existence of such a complex is quite possible since this combining ratio has been found for the amino acid—copper interaction in the pH range above 7.

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POTENTIOMETRIC STUDIES ON THORIUM TUNGSTATES

By

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[Received on 11th January, 1962]

ABSTRACT

The composition of thorium tungstates, obtained by the addition of thorium nitrate to a progressively acidified solution of sodium tungstate, has been studied by potentiometric method. From the results it is evident that five different tungstates of thorium can be obtained depending on the pH of the solution. It has been observed that the ageing effect is, to a great extent, responsible for the conflicting results obtained by different workers regarding the composition of the tungstates.

The effect of ageing on the polymerization of tungstic anhydride, when normal sodium tungstate solution is titrated against mineral acids, has been reported by Jander and Kruerke (1) and by Rao and Banerji (2). In the present studies it was investigated by adding regularly increasing instalments of nitric acid to a constant volume of sodium tungstate solution taken in different pyrex glass test tubes and determining the conductance of the supernatant liquid after (i) 0 hour, (ii) 24 hours, (iii) 3 days and (iv) 6 days and the pH after (i) 0 hour and (ii) 6 days. The breaks in the conductance curves and inflexions in the pH curves gave the ratio $\text{HNO}_3/\text{Na}_2\text{WO}_4$ as 1:1.0, 1:1.15, 1:1.33, 1:1.5 and 1:2.0 which suggested the possibility of the formation of different species at these points. Even at different concentration and age of the system the breaks in the curves, in general, remain at the same points showing that the principal species in the solution do not undergo any change. Nitric acid was added to different solutions of sodium tungstate according to the ratio mentioned above and then a metal salt was added to each to find out if the corresponding tungstate precipitated.

EXPERIMENTAL

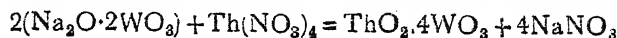
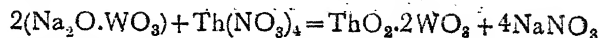
Standard solutions of A. R. quality reagents were prepared observing usual precautions. pH measurements were made with a direct reading Cambridge pH meter operated on 220V/50 cycles a. c. mains. The scale was calibrated with standard phthalate buffer before measurements and occasionally during the experiments. The electrodes were a wide range glass-calomel system supplied by the same manufacturer. The systems were maintained in a thermostatic bath maintaining temperature within $25.0 \pm 0.5^\circ\text{C}$.

10 ml of 0.1M sodium tungstate solution were taken in different pyrex glass test tubes. Required quantity of 0.25M nitric acid was added to each to have theoretically, as explained earlier, tungstate ions of a particular composition. 0.1M thorium nitrate solution was added from a micro-burette in regularly increasing instalments. The pH of these solutions, kept out of contact from atmospheric carbon dioxide, was noted after (i) 0 hour and (ii) 6 days. Titrations were performed with 0.067M and 0.05M sodium tungstate solutions also and the results were, in general, similar. The conclusions drawn from these results are supported by the conductometric and quantitative studies.

DISCUSSION

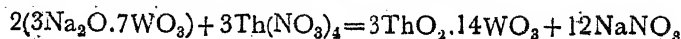
It is evident from the present studies that five different tungstates of thorium can be prepared by metathetic methods, using the interaction between sodium tungstate solution (containing varying amounts of nitric acid to form sodium tungstates in different degrees of polymerization) and thorium nitrate.

Normal and ditungstates of thorium are formed by direct interaction between thorium nitrate and the corresponding tungstate.

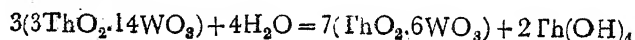


Ageing has no pronounced effect on the composition of these compounds.

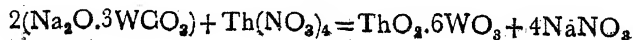
The paratungstate of thorium is also formed by direct interaction between thorium nitrate and the corresponding sodium tungstate.



In this case the amount of tungstic oxide associated with one mole of thorium oxide has a tendency to increase which is explainable on the basis of the hydrolysis of thorium paratungstate.

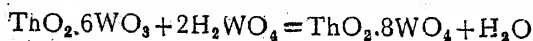
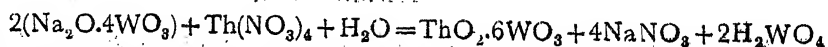


When sodium tritungstate reacts with thorium nitrate the thorium tritungstate is formed.



Ageing does not have much effect on this tungstate.

When sodium tetratungstate reacts with thorium nitrate, at first, thorium tritungstate is precipitated which, on ageing, gets converted into thorium tetratungstate.



ACKNOWLEDGEMENT

The author is grateful to Dr. S. Ghosh, D.Sc., F.N.I., F.N.A.Sc., Professor and Head of the Department of Chemistry and Dean of the Faculty of Science, University of Allahabad, for his guidance in this work.

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STUDIES ON SOME LESS FAMILIAR FERROCYANOGEN COMPLEXES, PART XIII: THE COLLOIDAL BEHAVIOUR OF Mo(VI) FERROCYANIDE

By

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[Received on 12th January, 1962]

ABSTRACT

Mo (VI) ferrocyanide sol of concentration upto 2 gm/litre was obtained by mixing the reactants in the molar ratio, Mo (VI) : FeCy_6^{-4} , 5:3. The same compound was obtained in the form of a gel by adding an excess of a highly concentrated solution of potassium ferrocyanide to a concentrated solution of molybdic acid with constant stirring. The resulting mixture set into a gel after about 48 hours. Several properties, studied during the sol-gel transformation revealed that the surface tension showed a continuous increase, while the pH remained almost constant for about 90 hours, after which there was a marked decrease in the surface tension and an increase in pH. Viscosity also showed an abnormal rise after more or less the same period. Conductivity variations were too small to give results of any value.

The composition and properties of molybdenum ferrocyanide have not yet been fully investigated. Experiments performed in these laboratories had shown that Mo(VI) with potassium ferrocyanide gives both soluble and insoluble compounds, their formation depending on the concentration of the reactants as well as the pH of the medium. Thus it was found that at ordinary concentration of the reactants in the pH range 2.9 to 3.8, a dark brown precipitate is obtained while in the pH range 4.0 to 5.2 a soluble complex is formed. It was also found that the interaction of the dilute solutions of the reactants (approx. M/500) resulted in the formation of a soluble complex (reddish brown in colour) of the composition¹ $(\text{MoO}_2)_2\text{FeCy}_6$ (employing Job's and limiting ratio methods) with an average value of $K = 1.55 \times 10^4$.

The problem of the existence of soluble metal ferrocyanogen complexes appears to be a controversial one. Compounds like Prussian and Turnbull's blues, chromic ferro- and ferricyanides², beryllium ferrocyanide³, although show semblance to many soluble complexes, their properties, especially the tendency to pass readily into colloidal state, leave some doubt regarding their true character. It was, therefore, thought worthwhile to carry out investigations on the colloidal behaviour of such compounds. The present communication deals with some aspect of the sol-gel transformation in molybdenum ferrocyanide.

EXPERIMENTAL

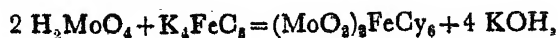
Solutions :

Molybdic acid solution was prepared by dissolving about 45.0 gms of molybdic acid (A. R.) in conc. HCl (free from iron) and making upto 500 cc with doubly distilled water. Its strength was determined by precipitating as PbMoO_4 and was found to be 0.6985M.

Potassium ferrocyanide solution was prepared by dissolving 196.0 gms. of recrystallised sample in conductivity water and making up to 500 cc. The solution was stored in dark bottles to avoid decomposition⁶ by sunlight. The strength was determined volumetrically against potassium permanganate of known strength. It was found to be 0.875M.

Molybdenum ferrocyanide sol :

Assuming that the reaction between Mo(VI) and K_4FeCy_6 takes place according to the equation :



the molar ratio of Mo(VI) : $FeCy_6$ would be 2:1, for the completion of the reaction. Attempts to prepare sols of even very low concentrations failed, when the reactants were mixed in this stoichiometric ratio. Many other combining ratios were then tried and it was finally found that a fairly stable sol of concentration upto 2 gms. per litre could be obtained by mixing the reactants in the molar ratio 5:3. Thus for preparing a sol of conc. 1 gm per litre, 6.12 cc. of 0.6985 M H_2MoO_4 and 3.14 cc. of 0.875 M K_4FeCy_6 were taken in separate vessels and diluted with doubly distilled water. Molybdic acid solution was then gradually added to potassium ferrocyanide solution with constant stirring. The volume was made upto 1000 cc. The resulting sol, dark red in colour was fairly stable and could be centrifuged without leaving any sedimentation. Sol of conc. 2 gms/litre was, however, not found to be so stable.

Prolonged dialysis of the sol destroyed its colloidal state. Even a dialysis period of four to five hours made the sol unstable. Addition of electrolytes to the sol dialysed for one hour resulted in clear separation of the layer between the two phases. Electrophoretic tube showed that the sol was negatively charged (electrode used were of platinum and a voltage of 140 volts D. C. was applied to them).

Sol-gel transformation in molybdenum ferrocyanide :

The usual methods, viz., those of evaporating or heating the given sol at a particular temperature, addition of appropriate amount of the electrolyte to the sol, or its prolonged dialysis, could not give the desired results with molybdenum ferrocyanide sol of strength upto 2.0 gms per litre. Mixing of the concentrated solution of the reactants followed by vigorous shaking of the resulting mixture (a method employed by us in preparing Prussian and Turnbells blues sols⁶) also failed in this case. After many trials, extending for several days we reached the following conclusion regarding the transformation of molybdenum ferrocyanide sol to a gel : (i) concentrations of the reactants, ranging between 0.1M to 0.5M, gave sols which coagulate in an hour to a few minutes (ii) with even large excess of potassium ferrocyanide, the concentration range given under (i) resulted in sols which did not transform into gel, instead a gelatinous precipitate was obtained, (iii) with very concentrated solutions, keeping the molar ratio near about 1:6 (Mo(VI) : $FeCy_6^{4-}$) which would change into a gel, could be obtained, under special conditions. The method followed was as under :

To 4 cc. of 0.6985 M H_2MoO_4 (taken in a dry beaker) 0.875M K_4FeCy_6 was added dropwise from a burette. After the addition of each drop the resulting

precipitate was rubbed vigorously for about ten minutes by means of glass rod. After the addition of about 20 cc. of potassium ferrocyanide in this way, it was possible to get a concentrated sol which would set to a gel in about two days. Unlike other metal ferrocyanide gels, it showed marked thixotropic properties. It was thus found that on shaking the gel for about thirty minutes it changed into a sol, which when left at room temperature got reconverted into a gel in about two hours.

Technique employed for studying gelations :

Variations in surface tensions during the transformation of the sol into gel were measured by means of Du Nouy apparatus. Conductivity measurements were carried out by an improvised Wheatstone bridge with a spread of 500 cms manganin wire (direct reading conductivity bridges failed to give reliable results with high conductance solution as employed here.) pH measurements during gelation were carried out by the help of Beckman pH meter Model H-2. Viscometric measurements were carried by means of Kopper's viscometer (constant pressure viscometer, or Scarpe's method using Ostwald viscometer failed to give satisfactory results.) The viscometer was connected to the vacuum reservoir and the stop cock opened. The time of rise between two predetermined points on the capillary was noted when carrying out a particular measurement. In this case points at 4 and 12 cms were selected (for materials of higher viscosity 2 and 4 cms, points in the capillary are taken). Sols A, B and C, prepared by mixing 40 cc. of 0.875M K_4FeCy_6 with 8.0 cc. 8.8 cc. and 9.6 cc. of 0.6985M H_2MoO_4 , respectively were used in these investigations. The results are depicted in Figs. 1, 2 and 3.

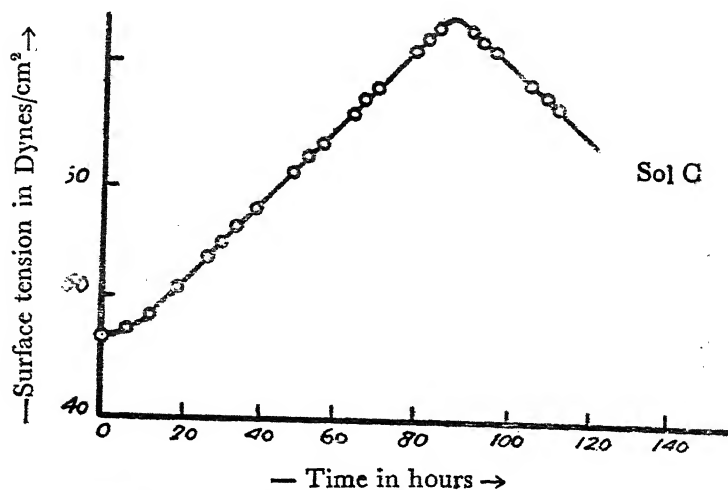
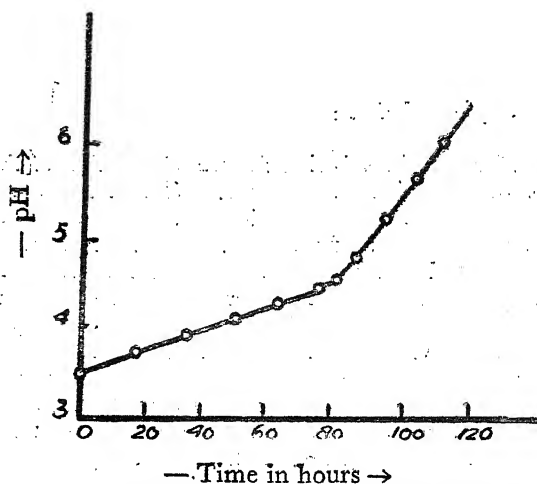


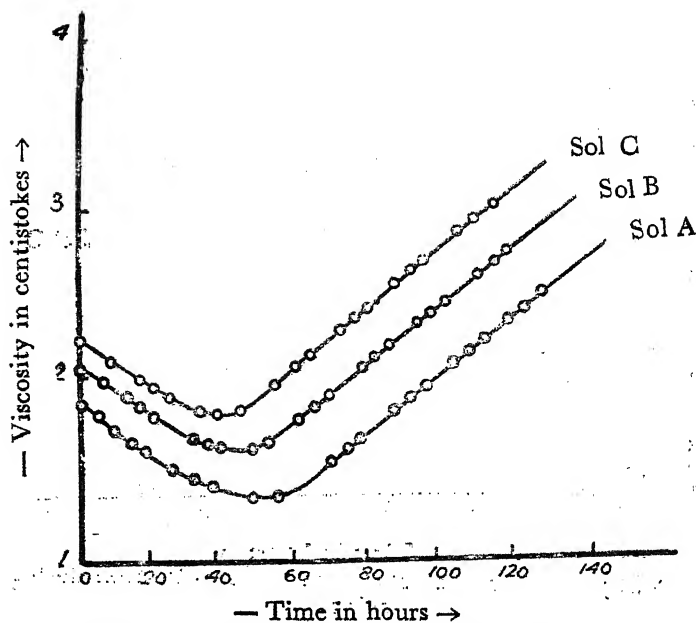
Fig. 1. Variation of surface tension with time during gelation.

DISCUSSION

Gel formation, in the case of molybdenum ferrocyanide, could not be realised by using any of the conventional methods used for obtaining inorganic gels. Even the method of mixing concentrated solutions (a modified method of von Weimarn's)



— Time in hours →
Fig. 2.—Variation of pH with time during gelation.



— Time in hours →
Fig. 3.—Variation of viscosity with time during Gelation.

of the reactants, as followed in the case of Iron blues (*loc. cit.*) and chromic ferrocyanide⁷ failed here. Considering von Weimarn's equation, it can be seen that the degree of dispersity, can be made large either by increasing P (degree or supersaturation) or L (the solubility). Since an increase in P (highly concentrated solutions being used in this case) results in the formation of gelatinous precipitate rather than a gel, the only other factor which could bring about an increase in the value of δ , and a consequent transformation of the sol into gel, can be L . It appears that with time the value of L slowly decreases and it is only after many hours that L adjusts itself in such a way that optimum condition for gel formation are well realised. Such a behaviour is not unlikely because it is a known fact that many freshly precipitated substances show a marked decrease in solubility on ageing.

The variations in surface tension during gelation (Fig. 1) show a continuous increase for about 90 hours, after which a marked decrease is observed. Such changes may be explained by assuming that in the early stage of transformation of the sol into the gel, the KOH obtained as the product of interaction as well as that of the decomposition of potassium ferrocyanide :



is gradually being entrenched by the developing gel structure. Only when gel formation has been completed (about 90 hours in the case of sol C) that the free base is available in the whole bulk, bringing about a sudden fall in the surface tension.

Results on the variations in surface tension find support in the pH measurements. From Fig. 2 it can be seen that for about ninety hours the changes in pH are very small (3.7 to 4.0) but later on there is a marked increase in pH, the change being equal to 1.0 unit in about twenty five hours.

Molybdenum ferrocyanide sols show marked variations in viscosity during gelation. From fig. 3 it is evident that only after about sixty hours that a gradual increase in viscosity (after the initial decrease) could be observed. This variation is, however, followed by a marked increase in viscosity after about 80 to 90 hours. The time after which the rapid increase in viscosity takes place may be taken as the time of gelation. The sudden increase in viscosity points towards a definite change from the sol state to that of the gel as has been observed by us while carrying out investigation on Iron blues, chromic ferrocyanide (*loc. cit.*) and tungstate gels.⁸ The only dissimilarity which has been observed here is that the decrease in viscosity is quite marked in the initial stages which is not the case in other inorganic gel forming mixtures. Furthermore, it is rather interesting to find that a sudden variation in any of the physical properties studied, *viz.*, surface tension, pH and viscosity takes place more or less after the same lapse of time, thereby showing that it can be taken as the measure of the time of gelation for the gel under consideration.

Of all the physical properties studied, variations in conductance were the least. In fact the conductivity remains almost constant throughout the process. These observations show that molybdenum ferrocyanide sol contains systems of capillary spaces filled with unchanged solvent.⁹

The time of setting of the gel for the three sols studied were 4 hours, 3 hours and 2 hours respectively. Those were determined by Fleming's method¹⁰ by allowing the gel to set after its structure had been disturbed on vigorous shaking.

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STUDIES OF RECTIFICATION IN AIR IN NEARLY UNIFORM FIELDS UNDER THE LOW FREQUENCY SILENT ELECTRIC DISCHARGE

By

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[Received on 27th January, 1960]

ABSTRACT

The paper reports observations of the discharge current and the rectification ratio in air under the low-frequency silent electric discharge using plane parallel glass electrodes over a range of pressure from 5 mm. Hg to 150 mm. Hg. The current potential characteristics exhibit three marked regions. The rectification ratio exhibits a series of maxima and minima with increasing potential. These results are discussed on the known hypotheses of rectification and the silent electric discharge.

INTRODUCTION

Rectification is a well known phenomenon in discharge studies and was observed as early as 1914 (Townsend, 1914) while studying positive and negative discharges from metallic points and cylinders. Later on (Thomson 1931, 39) it was shown that even when electrodes are similar, by adjusting the inter-electrode distance, current can be made to pass only one way when alternately one electrode is positive and negative. Koller (1937) explained this on the basis of cathode fall. Chiplonkar (1939, 41, 51) while working with Geissler tubes using plane similar metal electrodes, showed that if 50 cycles a. c. potential is applied, marked rectification could be observed which depended on pressure. He worked in the low pressure range of the order of 200×10^{-4} mm. Hg to 18 mm. Hg. Recently Talekar (1956, 57) worked in nitrogen under non-uniform fields using both full and semi ozonizers. He explained theoretically that if a. c. potentials are used, rectification is a pressure dependent phenomena and also is maximum at V_m . Most of the above studies refer to investigations under non-uniform fields. Little work appears to have been done using uniform fields. It was therefore of interest to investigate rectification in uniform fields. The present paper reports the studies of rectification in air using plane parallel glass electrodes.

EXPERIMENTAL

The general experimental arrangement is shown in fig. 1. The discharge tubes used were cylindrical glass tubes sealed at both the ends by two identical plane

glass plates. The inter-electrode distance in the two tubes reported here, was 3 cm. and 4 cm. respectively. Both the tubes were connected to the same feeder tube which was connected through a mercury manometer to the Duo Seal Vacuum pump. Dry air was admitted to the tubes which were then sealed at a desired pressure. The source of e. m. f. was a 20 kV transformer fed through a variac to which 220 volts, 50 cycles a. c. was applied. One glass-electrode was made H. T. while the other was earthed through a current detector. One terminal of the transformer was also earthed. The technique, to measure the potential applied to the tube was similar to that used by Thornton (1939). To measure the currents in both the halves of the a. c. cycle, a Pohl commutator was used as shown in Fig. 1. (The pressure range

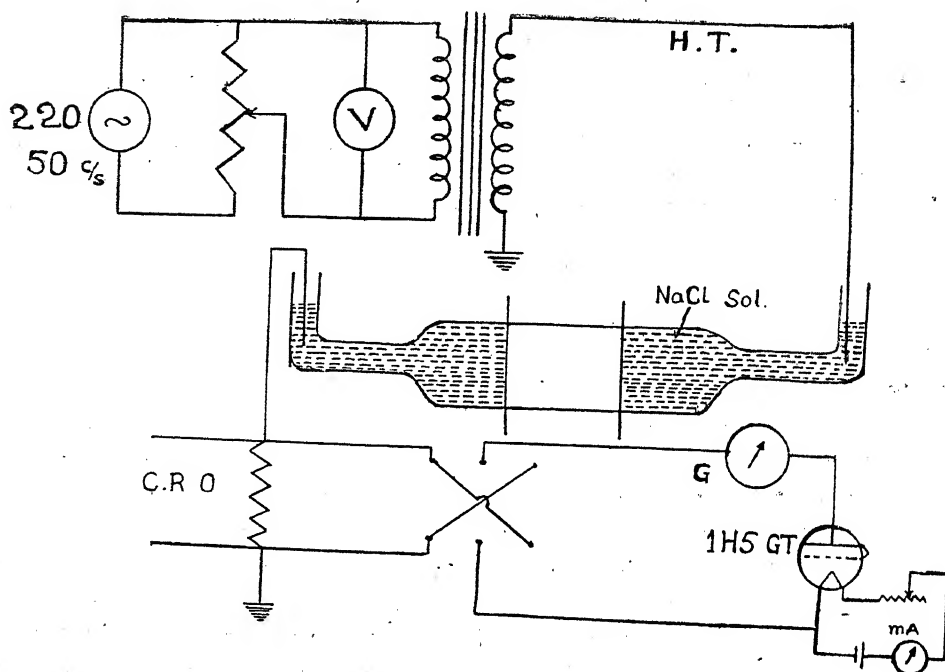


Fig. 1. The General Experimental arrangement.

covered in the present studies, varied from 5 mm. Hg to 147 mm. Hg) The current was measured by a sensitive moving coil galvanometer in the plate circuit of a detector (1 H 5 GT) connected to the L. T. line across a resistance. The wave pattern of the current was also investigated by feeding the potential drop across this resistance to the vertical input of cathode Ray-Oscillograph. Experiments undertaken with a view to check up the reproducibility of results, indicated that while there was some variation (app. 5%) in the values of the currents measured, the general variation of I as well as σ with potential was the same.

RESULTS

As the potential applied to the tubes is increased gradually from zero, a critical potential called the 'Threshold Potential V_m ' is reached, at which there is a sudden increase in the current flowing through the discharge tube. This is accompanied by the onset of the glow in the tube and the appearance of pulses on the current wave form. Fig. 2 shows the variation of V_m with the gas pressure P . It is seen that V_m varies sensibly linearly with pressure in accordance with Paschen's law. It is however concave to the pressure axis in the low pressure range from 5 mm. Hg to 20 mm. Hg.

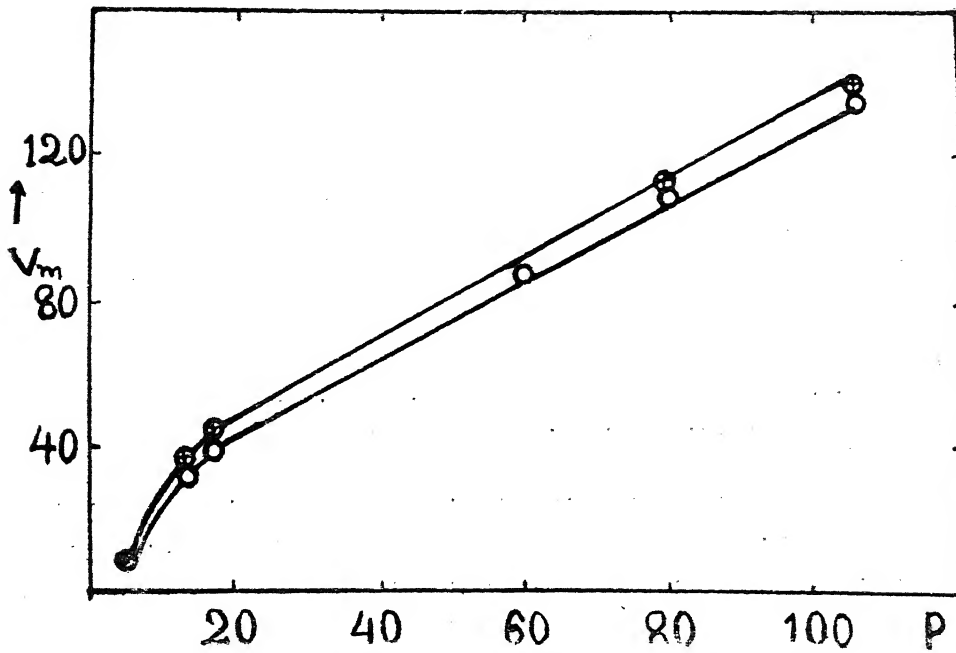


Fig. 2. Variation of the threshold potential V_m with the pressure of the gas P .

V_m in volts primary, P in mm. Hg.:

Upper curve for the large tube, turns ratio 90:9:1.

For pressures greater than 100 mm. Hg, a small capacitive current was observed below V_m , when a large input resistance was used. This capacitive current, however, was negligibly small for low pressures and with a low input resistance,

Fig. 3 shows the variation of the discharge current with the applied potential for the smaller tube in the negative half of the a. c. cycle. It is seen that as the

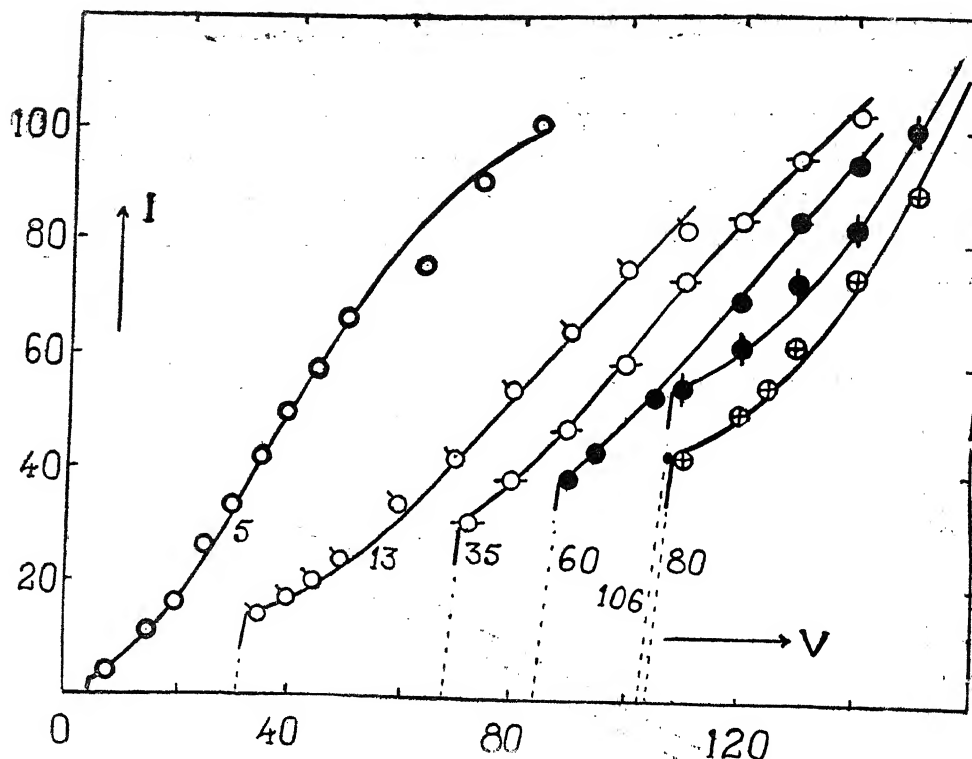


Fig. 3. Variation of discharge current I with the applied potential V .

Current I in arbitrary units, V in volts primary. Numbers on curves indicate pressure in mm. Hg.

potential is increased gradually above V_m , the discharge current exhibits two distinct regions. After the initial fast rise at V_m , the current sags with increasing voltage and then it rises again at higher potentials. This behaviour is shown by both the tubes and also in both the halves of the a. c. cycle. It is seen from Fig. 3 that, as the pressure increases, the initial region of fast rise at V_m also increases, while the intermediate region of slow rise or sagging portion decreases.

RECTIFICATION RATIO

The rectification ratio is defined as the ratio of the difference of the currents I_+ and I_- in the two halves respectively, to the total current $I_+ + I_-$ expressed as a percentage i. e. $\sigma = \frac{I_+ - I_-}{I_+ + I_-} \times 100$. The variation of this ratio with voltage for

the different pressures used is shown in fig. 4 and 5 for the two tubes respectively. It is seen that contrary to the results reported by Talekar (1956) the variation of σ with voltage does not follow a smooth curve, but exhibits a series of maxima and minima. Essentially similar results are reported by Chiplonkar (1939, 41) in his study of rectification at very low pressures, using metal electrodes. These maxima and minima are more marked for the smaller tube (more uniform field) than for the larger tube (less uniform field, *vide-infra*). As the potential applied to the tube is increased, the value of maxima and minima goes on diminishing and at very high potentials, it approaches the zero value. A comparison of the I - V curve with σ - V curve reveals close agreement, in respect of potential, between maximum (or minimum) of σ - V curve and a change in the slope of I - V curve. It is of interest to mention here that σ is not observed to be a maximum at V_m but at a potential slightly greater than V_m .

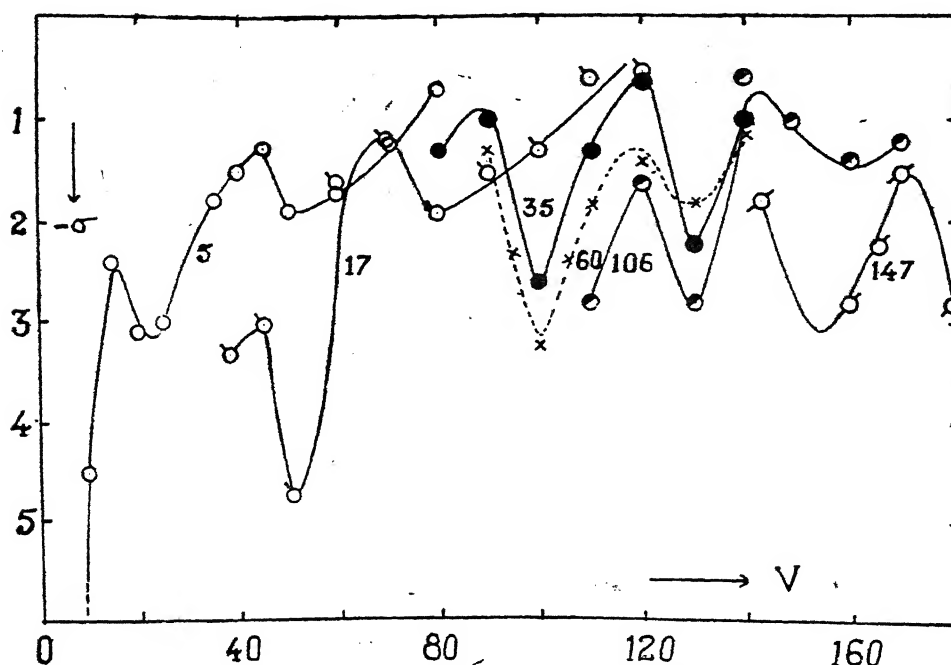


Fig. 4. Variation of rectification ratio σ with the applied potential for the small tube. V. Primary volts, σ in %. Numbers on curves indicate pressure in mm Hg.

VARIATION OF σ WITH PRESSURE

For the smaller tube, σ is found to be negative throughout the pressure range investigated. For the lowest pressure i. e. 5 mm. Hg, σ is observed to be optimum.

As the pressure is increased σ decreases from 7% at 5 mm. Hg to 3% at 147 mm. Hg. At other potentials the value of σ does not show any appreciable change with pressure. It is between 1 and 2%.

For the larger tube σ is also negative but it is smaller than that for the smaller tube. It is below 2% over most of the potential range.

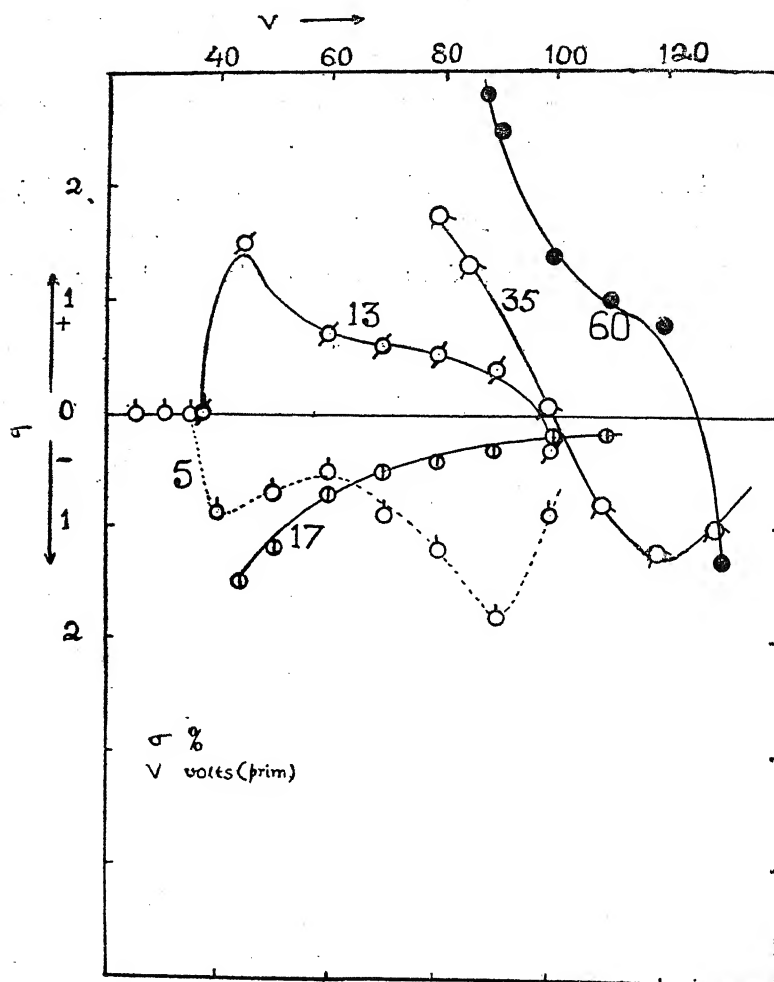


Fig. 5. Variation of rectification ratio σ with the applied potential V for the larger tube. V primary volts, σ in %, numbers indicate pressure in mm Hg.

DISCUSSION

The important role of the threshold potential V_m for the silent electric discharge and the chemical reactions was emphasised by Joshi (1939), who also suggested that V_m may be identical with, or simply related to, the corresponding Paschen potential,

That the Paschen's law holds good for the low frequency silent electric discharge in air, has been established recently in these laboratories (Jatar and Sharma, 1956). The present results are in accord with this.

The nature of the variation of the current with the applied potential reported here, is essentially similar to that reported for corona discharges. Detailed studies (Loeb and Miller, 1951) have shown that under d. c. corona, these three regions correspond essentially to the space charge free, the space charge limited and the steady corona regions. Essentially similar results have been reported for H_2 (Jatar 1958) and air (Sharma 1956) under the low frequency silent electric discharge.

In the present studies, however, the plane parallel electrodes of equal size were used and hence the field was, at least to a first approximation, uniform. It is of interest to mention here that for a strictly uniform field, the ratio of the electrode diameter, D , to the inter electrode distance, d , should be at least 3:1. In the present case, this ratio was only 1:1 or 2:3. It is not unlikely, therefore, that the field was slightly non-uniform. This non-uniformity was greater for the larger tube than for the smaller tube. While the observations of three distinct regions in the current potential characteristic may be partly due to the slight non-uniformity of the field in the present case, some other factor may also be responsible for the three regions mentioned above. Essentially similar results have been observed for the current potential characteristic under sleeve excitation (Jatar 1958).

As mentioned earlier, an attempt to explain rectification in uniform and non-uniform fields was first made by Koller (1937) who ascribed it to differences in the cathode fall. As shown by Talekar (1956), however, the rectification according to this hypothesis should be positive for non-uniform fields whereas a predominantly negative rectification was observed in N_2 . An explanation of rectification on the hypothesis of Koller, therefore does not appear to be likely.

To explain the results in N_2 , Talekar has recently proposed a hypothesis of rectification primarily for corona-discharges. He assumes the Werner's equation for the dependence of the discharge current I on the applied potential V and ascribes rectification essentially to the difference between the threshold potentials V_{m+} and V_{m-} in the two halves of the a. c. cycle. From this he shows that rectification should (1) be maximum at V_m and should decrease steeply and then slowly as the potential is increased above V_m (2) decrease as the gas pressure or the inter electrode distance is diminished. While this is suggested essentially for a semi-ozonizer having a large asymmetry in the size and also in the nature (metal and glass) of the two electrodes, the hypothesis has been extended to the cases of full ozonizers and also of Geissler tubes. In these latter cases it has been suggested by Talekar that rectification can be positive, zero, or negative according as $V_m - \begin{matrix} > \\ < \end{matrix} V_m +$. The whole hypothesis thus

predicts a difference in the starting potentials of the discharge in the two halves of the a. c. cycle, wherever rectification is observed. It is significant to note here that throughout the investigation reported here, as well as other detailed investigations carried out in these (Sharma 1956) and other laboratories (Joshi, 1947; Khastgir and Shetty 1952) on low frequency silent electric discharge, no difference was, at any time, observed in the starting potentials of the two halves. Even with cathode ray oscillograph, where the appearance of pulses is taken as a clear indication of the breakdown, the pulses were observed always simultaneously in both the halves. Moreover, the variation of rectification with the applied potential indicates that σ is not always maximum at V_m , a condition following naturally, from Talekar's hypothesis. An explanation of the present results therefore does not appear to be likely on Talekar's hypothesis.

The hypothesis of the low frequency silent electric discharge may now be considered. Deb and Ghosh (1946-47) and Harries and von Engel (1951) have suggested that this type of discharge consists of a series of pulses arising due to the starting and stopping of the discharge. These authors have emphasised the important role of the surface layer of electrons deposited on the glass walls and also of the positive ion-space charge. While the significance of the adsorbed layer on the glass electrodes has also been mentioned by these authors, no detailed mechanism for the secondary emission of electrons has been stated. Another hypothesis of the silent electric discharge was suggested from these laboratories (Jatar 1955, 1957). This hypothesis assumes that glass being a dielectric, the emission of electrons from glass under the conditions of study is not probable. The main source for the secondary emission of the electrons is the layer of the electrons deposited during the previous half cycle and not yet neutralised due to the dielectric nature of the glass. The energy of binding of these electrons to the glass is essentially low. Emission of electrons from this layer is envisaged both by ionic and electronic bombardments as well as by the photons.

According to all the above hypotheses no difference in V_{m+} and V_{m-} is to be expected at least for identical electrodes, as is actually found to be the case. Moreover, the current in a given half of the a. c. cycle will depend upon the number of electrons liberated and their progeny. The liberation of electrons as contemplated above, is however dependent on the effective work function* of the momentary cathode. It may be mentioned here that the importance of the work function of the cathode in rectification was also mentioned by Chiplonkar. Rectification will thus depend primarily on the effective work-function and the geometry of the tube. While a similar dependence has also been shown by Talekar for plane parallel-electrode s, his arguments and assumptions lead to the conclusion that, by this

*The term effective work function is used here loosely to indicate the energy of binding of the electrons to the electrode and does not indicate any mechanism similar to the photoelectric or thermionic work function.

difference in the effective work-function, the threshold breakdown potentials will be different in the two halves, as has never been observed. In the present case where the two electrodes are essentially identical, no rectification due to geometry factor is to be anticipated. The rectification that is observed, is thus entirely due to differences in the effective work function of the momentary cathodes.

It is significant to note here that, with a larger gap where the non-uniformity of the field would be greater, the variation of rectification with potential tends to approach that for non-uniform fields, as suggested by Talekar, namely it is maximum at V_m and tends to diminish to zero value at higher potentials. It is therefore suggested here that in any case, rectification should be considered as arising out of two independent factors: (1) differences in the work function of the cathode and (2) differences in the shape and size or geometry of the electrodes. The magnitude and sign of rectification under any given conditions will be the resultant of the rectifications observed on account of both these factors.

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THE MAGNETOGRAVITATIONAL INSTABILITY OF NON-UNIFORMLY ROTATING HOMOGENEOUS AND HEAT CONDUCTING MEDIUM

By

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[Received on 8th December, 1961]

ABSTRACT

In this paper the problem of gravitational instability of an infinite homogeneous, heat conducting and non-uniformly rotating medium in the presence of uniform magnetic field for axisymmetric perturbation is discussed. It is found that Pacholczyk and Stodolkiewicz's criterion of gravitational instability remains unaffected, even when the medium is heat conducting.

INTRODUCTION

Pacholczyk and Stodolkiewicz (1960) found that the Bel and Schatzman's (1958) criterion for gravitational instability of non-uniformly rotating homogeneous medium in the presence of magnetic field is modified to

$$4 \pi G \rho_0 > k^2 (V_a^2 + C^2) + \frac{2\omega}{r} \frac{d}{dr} (r^2 \omega) \quad \dots (1)$$

where V_a is Alfvén's velocity, $C = \sqrt{RT_0}$, is isothermal sound velocity, ω is angular velocity of rotation and other symbols have usual meanings. In the paper I (Anand and Kushwaha, 1962) it is shown that thermal conductivity of the medium does not modify the Bel and Schatzman's criterion. In the present paper an attempt has been made to study the effect of the presence of uniform magnetic field on the result of paper one.

2. Equations of the Problem :

Let us suppose that the frame of reference is so chosen that magnetic field \vec{H} in cylindrical coordinates is given by

$$\vec{H} = (0, H_\theta, 0) \quad \dots (2)$$

Assuming that the perturbed quantities are functions of r only, the perturbed, linearized equations of the problem under the usual hydromagnetic assumption are :

$$\begin{aligned} \rho_0 \frac{\partial u}{\partial t} = & - \frac{\partial}{\partial r} \delta p - \frac{H_\theta}{4\pi r} \frac{\partial}{\partial r} (r h_\theta) - \frac{h_\theta}{4\pi r} \frac{\partial}{\partial r} (r H_\theta) \\ & + 2 \rho_0 v \omega + \rho \frac{\partial \delta V}{\partial r} \end{aligned} \quad \dots (3)$$

$$\rho_0 \frac{\partial v}{\partial t} = \rho_0 u F + \frac{h_r}{4\pi r} \frac{\partial}{\partial r} (r H_\theta) \quad \dots (4)$$

$$\text{with } F = -\omega - \frac{d}{dr} (r\omega) \quad \dots (5)$$

$$\frac{\partial h_\theta}{\partial t} = -H\theta \frac{\partial u}{\partial r} - u \frac{\partial H\theta}{\partial r} \quad \dots (6)$$

$$\frac{\partial h_r}{\partial t} = 0 \quad \dots (7)$$

Equation of Continuity :

$$\frac{\partial}{\partial t} \delta\rho + \rho_0 \frac{\partial u}{\partial r} + \frac{\rho_0 u}{r} = 0 \quad \dots (8)$$

$$\frac{\partial}{\partial r} (r h_r) = 0 \quad \dots (9)$$

Poisson's Equation :

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \delta V}{\partial r} \right) = -4\pi G \delta\rho \quad \dots (10)$$

Equation of Energy :

$$\rho_0 C_p \frac{\partial}{\partial t} \delta T - \frac{\partial}{\partial t} \delta p = \frac{K}{r} \frac{\partial}{\partial r} \left[r \frac{\partial \delta T}{\partial r} \right], \quad \dots (11)$$

$$\text{with } \frac{\delta p}{\rho_0} = \frac{\delta\rho}{\rho_0} + \frac{\delta T}{T_0} \quad \dots (12)$$

where u and v are perturbed radial and tangential components of velocity, δp , $\delta\rho$, δT , δV , h_r and h_θ are perturbed pressure, density, temperature, gravitational potential, radial and tangential components of magnetic field, K is thermal conductivity of the medium, other symbols have usual meanings.

Now from equations (9) and (7), we get

$$h_r = \text{Const.} = 0 \text{ (say)}. \quad \dots (13)$$

Eliminating δT from (11) and (12) we get

$$\frac{\partial}{\partial t} (\delta p - C^2 \delta\rho) = \frac{K}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (\delta p - C'^2 \delta\rho) \right], \quad \dots (14)$$

$$\text{where } C^2 = \gamma R T_0, \quad C'^2 = \frac{K}{\rho_0 C_p} \quad \dots (15)$$

which are taken constant in the following work.

We consider solution of equations, (3), (4), (6), (8), (10) and (14) with a time-dependent factor in the form $\exp \sigma t$. Thus we can write perturbed quantities as

$$f(r, t) = f(r) \exp \sigma t \quad \dots (16)$$

where σ is related to the frequency of perturbation. Putting (16) in (8) and (10) and integrating, we get

$$u(r) = - \frac{\sigma}{\rho_0 r} \int_{r_0}^r x \delta \rho(x) dx, \quad \dots (17)$$

and

$$\frac{d}{dr} \delta V = - \frac{4\pi G}{r} \int_{r_0}^r x \delta \rho(x) dx. \quad \dots (18)$$

Using (16) in (3), (4) and (6), and eliminating h_θ and v we get,

$$\begin{aligned} \rho_0 \sigma u = & \frac{H_\theta^2}{4\pi\sigma} \frac{d^2 u}{dr^2} + \frac{1}{4\pi\sigma} \left[\frac{2H_\theta^2}{r} + 3H_\theta \frac{dH_\theta}{dr} \right] \frac{du}{dr} \\ & + \frac{1}{4\pi\sigma} \left[\left(\frac{dH_\theta}{dr} \right)^2 + \frac{2H_\theta}{r} \frac{dH_\theta}{dr} + H_\theta \frac{d^2 H_\theta}{dr^2} \right] u \\ & + \frac{2\rho_0 \omega}{\sigma} F u + \rho_0 \frac{d\delta V}{dr} - \frac{d}{dr} \delta p \end{aligned} \quad \dots (19)$$

Let us suppose that the magnetic field is uniform i.e. H_θ is constant and then for uniform magnetic field, (19) can be written as

$$\begin{aligned} \rho_0 \sigma u = & \frac{H_\theta^2}{4\pi\sigma} \frac{d^2 u}{dr^2} + \frac{1}{4\pi\sigma} \frac{2H_\theta^2}{r} \frac{du}{dr} + \frac{2\rho_0 \omega}{\sigma} F u \\ & + \rho_0 \frac{d\delta V}{dr} - \frac{d}{dr} \delta p \end{aligned} \quad \dots (20)$$

Eliminating u , $\frac{d\delta V}{dr}$ from equation (20) by using (17) and (18), we get

$$V_a^2 \frac{d^2 P}{dr^2} + \left(2\omega F + 4\pi G \rho_0 - \sigma^2 \right) P + r \frac{d\delta p}{dr} = 0, \quad \dots (21)$$

where

$$P(r) = \int_{r_0}^r x \delta \rho(x) dx, \quad \dots (22)$$

$$V_a^2 = \frac{H_\theta^2}{4\pi\rho_0} \quad \dots (23)$$

Also putting (16) and (22) in (14) we get

$$\sigma \left(\delta p - \frac{C^2}{r} \frac{dP}{dr} \right) = \frac{\bar{K}}{r} \frac{d}{dr} \left[r \frac{d}{dr} \left(\delta p - \frac{C^2}{r} \frac{dP}{dr} \right) \right]. \quad \dots (24)$$

Equations (21) and 24) are dispersion relations for this problem.

To investigate the local instability in the neighbourhood of $r = r_0$, following paper I, we get the final equation as follows :

$$\sigma^3 + (\bar{K} k^2) \sigma^2 + (V_J) \sigma + (\bar{K} k^2) V_J' = 0, \quad \dots (25)$$

where

$$\begin{aligned} V_J &= k^2 (V_a^2 + C^2) - 2 \omega F - 4 \pi G \rho_0 \\ V_J' &= k^2 (V_a'^2 + C'^2) - 2 \omega F - 4 \pi G \rho_0 \end{aligned} \quad \dots (26)$$

3. Condition for Gravitational Instability

Hurwitz criterion is applied to get the condition of gravitational instability. The necessary and sufficient, condition for stability has been discussed by Guillemin (1950). The necessary condition for stability is that all the coefficient in the secular equation should be positive. This condition means that the real part of σ will be negative. In our secular equation all the coefficients are positive if

$$V_J' > 0$$

But when $V_J' < 0$ then at least the constant term in (25) is negative. Therefore, for instability of the medium, we have the following criterion.

$$4 \pi G \rho_0 > k^2 \left(V_a^2 + C'^2 \right) + \frac{2 \omega}{r} \frac{d}{dr} (r^2 \omega) \quad \dots (27)$$

Hence it is seen that the Pacholczyk and Stodolkiewicz's criterion is unaffected by thermal conductivity.

Thus from this and the previous work it can be concluded that the effect of thermal conductivity is to replace the adiabatic sound velocity by the isothermal sound velocity and for the cases of isothermal medium where the sound velocity is already isothermal sound velocity, no effect is found.

ACKNOWLEDGEMENTS

One of the authors (S. P. S. Anand) wishes to express thanks to the Council of Scientific and Industrial Research for the financial support of this work.

We are also thankful to Mr. P. K. Raju for his helpful discussions.

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ON THE ASYMPTOTIC BEHAVIOUR OF SOLUTIONS OF NON-LINEAR DIFFERENTIAL EQUATIONS

By

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[Received on 22nd December, 1961]

§1.

V. Lakshmi Kanth [1] has established some results concerning the asymptotic behaviour of solutions of

$$\frac{dx}{dt} = f(t, x) \quad \dots (1.1)$$

In this note we obtain similar results with less restrictive assumptions. In §2 we establish a lemma concerning (1.1) using the notion of maximal solution, which in turn will be employed for obtaining the results in §3 concerning the boundedness and the asymptotic behaviour of the solutions of (1.1). In §4 we obtain a theorem on the comparison of the solutions of two different systems of equations.

§2.

We consider the system of differential equation (1.1) where x denotes a n -dimensional Vector and $f(t, x)$ is a given vector field which is defined in the product space $\Delta = I \times R^n$ and is continuous in Δ , where I is the interval $0 \leq t < \infty$ and R^n is Euclidean space of n dimensions.

Let $V(t, u(t)) \geq 0$, be a scalar function also defined on Δ . We assume that V satisfies a Lipschitz condition in u locally. We define

$$V^*(t, u(t)) = \lim_{h \rightarrow 0} \sup_{+} \frac{1}{h} [V(t+h, u) - V(t, u)] \quad \dots (2.1)$$

Lemma.

Let $\omega(t, r)$ be defined on $0 \leq t < \infty$, $r \geq 0$, continuous in r for fixed t and measurable in t for fixed r . Suppose

$$V^*(t, u) \leq \omega(t, V(t, u)) - \alpha V(t, u) \quad \dots (2.2)$$

where α is a suitably chosen positive number.

Further let

$$|f(t, x_1) - f(t, x_2)| \leq V(t, x_1 - x_2) \quad \dots (2.3)$$

where $|x|$ indicates the Euclidean norm of x .

$$\text{Let } r(t) \text{ be the maximal solution of } r' = \omega(t, r) \quad \dots (2.4)$$

with $r(t_0) \leq r_0$, $r_0 > 0$. Then if $x_1(t)$ and $x_2(t)$ are any two solutions of (1.1), setting $u(t) = x_1 - x_2$, we have

$$V(t, u) \leq r(t), \text{ for } t \geq t_0. \quad \dots (2.5)$$

Proof:

As V satisfies a Lipschitz condition in u we have

$$\begin{aligned} & V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) - V(t, u) \\ = & V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) - V(t+h, u) + V(t+h, u) - V(t, u) \\ \leq & K|h\{f(t, x_1) - f(t, x_2)\}| + V(t+h, u) - V(t, u) \end{aligned} \quad \dots (2.6)$$

where K is some constant.

Therefore from (2.2), (2.3) and (2.6) we have

$$\lim_{h \rightarrow 0} \sup. \frac{1}{h} [V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) - V(t, u)] \leq \omega(t, V(t, u)) \quad \dots (2.7)$$

Let $x_1(t)$ and $x_2(t)$ be any two solutions of (1.1).

Define $V(t, u) = m(t)$, then we have for sufficiently

Small ε_1 and ε_2 where $\varepsilon_1 > 0$ and $\varepsilon_2 > 0$,

$$\begin{aligned} & \frac{x_1(t+h) - x_1(t)}{h} = f(t, x_1) + \varepsilon_1 \\ \text{and } & \frac{x_2(t+h) - x_2(t)}{h} = f(t, x_2) + \varepsilon_2, \\ \text{i.e. } & \frac{u(t+h) - u(t)}{h} = f(t, x_1) - f(t, x_2) + \varepsilon_1 - \varepsilon_2. \end{aligned} \quad \dots (2.8)$$

Again

$$\begin{aligned} m(t+h) - m(t) &= V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) + h(\varepsilon_1 - \varepsilon_2) \\ &- V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) \\ &+ V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) - V(t, u) \\ &\leq K|h(\varepsilon_1 - \varepsilon_2)| + V(t+h, u+h\{f(t, x_1) - f(t, x_2)\}) \\ &- V(t, u). \end{aligned}$$

Therefore we get

$$\lim_{h \rightarrow 0} \sup. \frac{1}{h} [m(t+h) - m(t)] \leq \omega(t, m(t)) \quad \dots (2.9)$$

Now suppose that $b(t, y)$ is a solution of

$$r' = \omega(t, r) + y, y > 0, \text{ with } r(t_0) \leq r_0, r_0 > 0.$$

We will show that

$$m(t) \leq b(t, y) \text{ for } t \geq t_0. \quad \dots (2.10)$$

For suppose (2.10) does not hold. Then without loss of generality, let (t_0, t_1) be an interval where $m(t) \geq b(t, y)$. At $t = t_0$ we have $m(t_0) = b(t_0, y)$. Taking the right hand derivative at t_0 we have $m'(t_0) \geq b'(t_0, y)$, but from (2.9) $\omega(t_0, m(t_0)) \geq \omega(t_0, b(t_0, y)) + y$

which leads to a contradiction as $m(t_0) = b(t_0, y)$.

This proves (2.10).

$$\lim_{y \rightarrow 0} b(t, y) = r(t) \quad [2]$$

This proves the lemma.

§ 3.

Theorem 1. Let

(i) $|f(t, x_2) - f(t, x_1)| \leq V(t, x_1 - x_2)$, where V satisfies the conditions of the lemma,

(ii) $r(t)$ be the maximal solution of $r' = \omega(t, r)$ and

$$(iii) \int_{t_0}^{\infty} r(t) dt < \infty,$$

then if one solution of (1.1) tends to a finite limit as t tends to infinity, then every solution of (1.1) also tends to a finite limit asymptotically. If, further, for sufficiently large t ,

$$(iv) \int_{t_0}^t r(t) dt < \varepsilon, \text{ where } \varepsilon > 0 \text{ is an arbitrarily small number,}$$

then every solution of (1.1) tends to the same limit asymptotically.

Proof :

Let $x_1(t)$ and $x_2(t)$ be any two solutions of (1.1)

Set $u(t) = x_1 - x_2$. Then

$$\begin{aligned} |u(t)| &= |x_1 - x_2| \leq \int_{t_0}^t |f(s, x_1) - f(s, x_2)| ds \\ &\leq \int_{t_0}^t V(s, u) ds \\ &\leq \int_{t_0}^t r(s) ds. \end{aligned}$$

The theorem follows with the assumptions made above.

Remark :

If we put $f(t, v) \equiv 0$, then every solution tends to a finite limit as $t \rightarrow \infty$. Hence the following theorem holds.

Theorem 2. If

$$(i) \quad |f(t, x)| \leq V(t, x)$$

(ii) $\int_{t_0}^{\infty} r(t) dt < \infty$, then the norm of every solution of (1.1) tends to a finite limit

asymptotically. If in particular for large t ,

(iii) $\int_{t_0}^t r(t) dt < \varepsilon$, where $\varepsilon > 0$ is arbitrarily small, then each component of

every solution of (1.1) tends to zero asymptotically.

The proof is similar to Theorem 1.

§ 4.

Theorem 3.

Let $\frac{dx}{dt} = f(t, x)$ and $\frac{dz}{dt} = g(t, z)$ be two systems of equations where f and g are vector fields defined on Δ as specified in the lemma and continuous there. Further, let $|f(t, x) - g(t, z)| \leq V(t, x - z)$, and $r(t)$ be the maximal solution of $r' = \omega(t, r)$, where $V(t, u)$ and $\omega(t, r)$ satisfy the conditions of the lemma. Then

if $\int_{t_0}^{\infty} r(t) dt < \infty$ and if one solution of one system tends to a finite limit as $t \rightarrow \infty$,

then every solution of the other system tends to a finite limit asymptotically.

If further, for sufficiently large values of t

$\int_{t_0}^t r(t) dt < \varepsilon$, where $\varepsilon > 0$ is arbitrarily small, then every solution of both the

systems tends to the same limit asymptotically.

The proof is similar to that of theorem 1.

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STABILITY OF LYOPHOBIC SOLS

PART XII. THE EFFECT OF TEMPERATURE ON THE STABILITY OF HYDROUS FERRIC OXIDE SOL WITH REFERENCE TO THE EFFECT OF NON-ELECTROLYTES

By

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[Received on 1st February, 1961]

ABSTRACT

The time of complete coagulation has been noted at three temperatures for hydrous ferric oxide sol in the absence and in the presence of non-electrolytes. For ethyl alcohol, acetone and gelatin, which sensitise the sol, the energy of activation and the steric factor decrease for certain amount of coagulating electrolyte. For glucose and urea causing stabilisation the reverse happens. It has been concluded that the effect of non-electrolyte towards the stability of the sols is mainly due to the modification of surface properties of the dispersed particles by the added non-electrolyte.

INTRODUCTION

Ghosh¹ has emphasised the importance of temperature in defining the stability of a sol. Here we have studied the coagulation values of potassium nitrate and potassium sulphate at three temperatures and the data thus obtained has been utilised in the calculation of energy of activation (E) and the relative change in the value of steric factor (p) both in the absence and in the presence of non electrolytes.

Assuming the process of coagulation as analogous to a chemical reaction Ghosh² has suggested the equation

$$\log t = \frac{E}{2.303 RT} - \log kpz \quad \dots (1)$$

By plotting $\log t$ against $1/T$, a straight line is obtained, the slope of the line gives the value of $E/2.303 R$. On substituting the value of E in equation (1) the value of $\log kpz$ is obtained. Variation in the value of kpz may be attributed to the change in the value of p , z , or both. When a definite quantity of a sol is coagulated by different amounts of an electrolyte, we may assume that a particular stage of aggregation is reached where coagulation is observed. We may here consider that the average value of z remains the same. In such a case we may ascribe any variation in the value of kpz to the change in the value of p . When, however, the average size of the dispersed particles (such as sols A, B and C) are different, the values of z are not the same and hence the values of kpz have not been calculated. It is possible to compare the values of kpz and attribute its change for a sol of same concentration to the variation in the value of p .

EXPERIMENTAL

Positively charged sol of hydrous ferric oxide was obtained by peptising freshly precipitated and thoroughly washed precipitate of ferric oxide by HCl. The precipitate was shaken with the acid, at a constant speed by Microid shaker till a brick

red sol was obtained which was centrifuged at three speeds namely 6,000 r. p. m., 14,000 r. p. m. and 22,000 r. p. m., to get the samples A, B and C respectively varying in average size of the dispersed particles. The samples were made to contain the same amount of Fe^{+++} /lit. The purity of the sol has been given by the ratio $\text{Fe}_2\text{O}_3/\text{Cl}^-$.

2.0 ml. of the sol was taken in each set of test tubes. Different amounts of coagulating electrolyte made up to 13.0 ml. with distilled water were taken in another set and kept in a precision thermostat, till they attained the temperature of the bath. The contents were mixed and the time of complete coagulation was noted at the visual separation of the clear liquid at the upper surface of the test tube. Similar studies were done in the presence of a known amount of non-electrolyte keeping the total volume the same (15.0 ml.). The observations have been recorded at three temperatures *viz.* 35°, 40° and 45°C.

Coagulation with Potassium nitrate

TABLE 1

Concentration of the sol A = S (0.8032 gm. Fe_2O_3 /lit.)

Purity of the sol = 3.585

0.2N KNO_3 ml.	log t			$\frac{E}{K. Cal.}$
	35°C	40°C	45°C	
8.0	3.1553	2.9542	2.7853	17.280
7.0	3.2253	3.0531	2.8805	16.120
6.0	3.2833	3.1531	2.9808	14.920
5.0	3.4409	3.2945	3.1461	14.050
4.0	3.5562	3.4048	3.2648	13.130

TABLE 2

Concentration of the sol B = S

Purity of the sol = 3.585

0.2N KNO_3 ml.	log t			$\frac{E}{K. Cal.}$
	35°C	40°C	45°C	
8.0	3.2355	3.0531	2.8751	16.350
7.0	3.2788	3.1038	2.9435	15.200
6.0	3.3444	3.1931	3.0334	14.280
5.0	3.4955	3.3541	3.2041	13.130
4.0	3.6434	3.5132	3.3766	12.440

TABLE 3

Concentration of the sol $C = S$ Purity of the sol $= 3.584$

K0.2N NO ₃ ml.	log t			$\frac{E}{K. Cal.}$	log $k_p z$
	35°C	40°C	45°C		
8.0	3.3201	3.1461	2.9854	15.660	7.719
7.0	3.3404	3.1818	3.0212	15.510	6.889
6.0	3.4133	3.2525	3.1139	13.590	6.166
5.0	3.5762	3.4378	3.3054	12.440	5.189
4.0	3.7488	3.6294	3.4900	11.740	4.524

TABLE 4

Concentration of the sol $C = S$ Purity of the sol $= 3.584$

0.2N KNO ₃ ml,	$\frac{E}{K. Cal.}$				
	3.0% ethyl alcohol	3.0% acetone	3.0% glucose	3.0% urea	0.0003% gelatin
8.0	14.740	14.280	16.120	16.120	15.200
7.0	13.820	13.360	14.970	14.740	14.050
6.0	12.900	12.440	14.050	13.820	13.130
5.0	11.980	11.050	12.900	12.670	11.980
4.0	11.050	10.590	12.216	11.980	11.280

TABLE 5

Concentration of the sol $C = S$
Purity of the sol $= 3.584$

0.2N KNO_3 ml.	$\log k_{pz}$				
	3.0% ethyl alcohol	3.0 % acetone	3.0% glucose	3.0% urea	0.0003% gelatin
8.0	7.549	7.507	7.978	7.991	7.577
7.0	6.846	6.796	7.096	7.004	6.753
6.0	6.093	6.068	6.410	6.252	5.984
5.0	5.172	5.011	5.334	5.265	5.024
4.0	4.329	4.450	4.622	4.640	4.514.

Coagulation with Potassium sulphate

TABLE 6

Concentration of the sol $= S^1$ (1.623 gm. Fe_2O_3 /lit.)

Purity of the sol $= 2.06$

0.0005N K_2SO_4 ml.	$\frac{E}{K. Cal}$			
	Sol A	Sol B	Sol C	$\log k_{pz}$ Sol C
8.2	16.120	15.200	14.510	6.751
8.0	15.660	14.740	14.050	6.354
7.8	15.200	14.280	13.820	6.123
7.6	14.740	13.820	13.130	5.586
7.4	14.050	13.130	12.440	5.065

TABLE 7

Concentration of the sol $C = S^1$

Purity of the sol = 2.06

0.0005N K_2SO_4 ml.	E K. Cal.				
	3.0 % ethyl alcohol	3.0% acetone	3.0% glucose	3.0% urea	0.0003% gelatin
8.2	13.360	12.900	14.970	15.200	14.050
8.0	12.670	12.210	14.510	14.970	13.590
7.8	12.440	11.980	14.280	14.740	13.130
7.6	11.740	11.280	13.590	14.050	12.440
7.4	11.050	11.050	12.900	13.360	11.980

TABLE 8

Concentration of the sol $C = S^1$

Purity of the sol = 2.06

0.0005N K_2SO_4 ml.	$\log k_{pz}$				
	3.0% ethyl alcohol	3.0% acetone	3.0% glucose	3.0% urea	0.0003% gelatin
8.2	6.749	6.596	6.916	6.881	6.542
8.0	6.193	6.028	6.536	6.612	6.075
7.8	5.987	5.776	6.306	6.353	5.752
7.6	5.439	5.239	5.768	5.838	5.167
7.4	4.913	5.032	5.239	5.111	4.781

TABLE 9

Potassium nitrate Sol A (0.0032 gm. Fe_2O_3 /lit.)		Potassium sulphate Sol A (1.623 gm Fe_2O_3 /lit.)	
log C	log $k_p z$	log C	log $k_p z$
0.9031	9.015	0.9138	7.927
0.8451	8.135	0.9031	7.537
0.7762	7.267	0.8921	7.136
0.6990	6.459	0.8808	6.726
0.6021	5.697	0.8692	6.247

DISCUSSION

The following conclusions are drawn from the observations :—

(1) The energy of activation (E) increases with the increasing size of the dispersed particles and with the increasing concentration of added electrolyte.

(2) In the presence of ethyl alcohol, acetone and gelatin which have been reported³ to sensitise the sol, the value of E decreases whilst it increases in the presence of glucose and urea causing stabilisation⁴ for a certain concentration of coagulating electrolyte.

(3) The relative value of steric factor (p) increases with the increasing amount of added electrolyte and varies directly with the concentration of coagulating electrolyte.

(4) The relative value of p decreases in the presence of ethyl alcohol, acetone and gelatin whilst it increases in the presence of glucose and urea.

It may, therefore, be concluded that smaller sized colloidal particles, because of their greater free surface energy, require smaller energy of activation for their aggregation than the coarser ones. It is well known that in a rate process, which is a contribution of several processes, the slowest one determines the rate. In coagulation process, when larger amounts of an electrolyte are used, the rate of aggregation becomes fast because of the considerable decrease in electric charge on colloidal particles but it becomes very slow as it approaches the state of flocculation; hence the later stage of aggregation determines the rate. The energy of activation, therefore, increases with the increasing concentration of the coagulating electrolyte.

For sensitisation, the non-electrolyte increases the cohesive forces of the dispersed particles, hence for the same amount of the coagulating electrolyte, the value of E is decreased. The reverse happens for stabilisation.

According to the theory of 'Absolute Reaction Rate' p is proportioned to ΔS or change in entropy to form the intermediate complex. The value of ΔS in the formation of transitory complex decreases when the colloid particles collide to form aggregated

particles. This is prominent for a sol when smaller quantities of electrolyte are added to it. We are, therefore, of the opinion that the value of p is related with the electrical properties of the dispersed matter.

For sensitisation ΔS decreases which implies that the residual charge of the colloidal particles increases and for stabilisation, the reverse is observed.

In the presence of a non-electrolyte causing sensitisation, the residual charge on the particles increases yet the rate of coagulation becomes fast.

For stabilisation, the reverse happens. We are, therefore, of the opinion that the effect of a non-electrolyte on the stability of the sols is mainly due to the modification of the surface properties of the dispersed particles by the added non-electrolyte.

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KINETICS OF THE REDUCTION OF CERIC SULPHATE BY GLYCEROL

By

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[Received on 22nd February, 1962]

ABSTRACT

In the present work glycerol is oxidised to different stages. The number of equivalents of ceric sulphate consumed by one mole of glycerol were determined. The total reaction is found to be of second order. The effect of sulphuric acid concentration was investigated which is inversely proportional to the specific rate of the reaction. The temperature coefficient was found to be unusually high. The heat of activation was calculated, which increases with increasing temperature.

INTRODUCTION

Cr (VI) and Mn (VII) in the form of chromates and permanganates are common oxidising agents. During the reduction of their compounds to the lower valency states they pass through a number of intermediary ones, so that the course of the reaction and its mechanism usually becomes a complicated process. Ce^{+4} and Mn^{+3} , however, on reduction to trivalent and bivalent states respectively involve only one electron transfer, and therefore the reaction mechanism may be simpler. Both of these two oxidising agents are to be prepared in strong acid solution. Ceric salt solution is stable in acid for an indefinite period. Its oxidising capacity is also not affected by the common impurities found in ceric salts. Ce^{+4}/Ce^{+3} oxidation potential is high and therefore it is a good oxidising agent.

Oxidation of a number of organic acids, aliphatic ketones and aldehydes by ceric sulphate have been studied by various workers (1). Very recently Mehrotra and Ghosh (2) studied the kinetics of oxidation of tartaric and citric acids, fructose and glucose. In all these cases the formation of the intermediary complex has been suggested. Sharma and Mehrotra (3) have oxidised glycerol by refluxing it with an acidified ceric salt for ten minutes and reported that 8.0 equivalents of Ce^{+4} are used up for the oxidation of one mole of glycerol.

This paper deals with the study of the kinetics of oxidation of glycerol solution by ceric sulphate solution.

EXPERIMENTAL

A stock solution of Ce (IV) sulphate was prepared in sulphuric acid (B. D. H. sample A. R.) and it was standardised by a standard solution of ferrous ammonium sulphate. Solution of glycerol (Analar B. D. H. quality) was prepared by direct weighing but the solution was finally standardised against standard solution of potassium dichromate. At first the equivalents of Ce^{+4} required to oxidise one mole of glycerol were determined. For this purpose, the two solutions *viz.*, ceric salt and glycerol were mixed together in different proportions in conical flasks and were kept at 30°, 40°, 50°, 70°C for over twenty four hours and also refluxed at 98°C for several hours. The concentration of Ce (IV) sulphate was always more than 14 times the concentration of glycerol. The unused ceric sulphate was estimated volumetrically against ferrous ammonium sulphate. Results are recorded in table 1.

TABLE 1

Temp.	Conc. of Ce (IV) Sulphate (M)	Conc. of glycerol (M)	Conc. of sul- phuric acid (N)	No. of equi- valents of Ce ⁺⁴ used for 1 mole of glycerol.
30°C	0.01515	0.00116	0.40	3.45
	0.02020	0.00116	0.40	3.60
	0.02525	0.00116	0.40	3.50
			Average	... 3.51
40°C	0.01250	0.00075	0.40	4.87
	0.01875	0.00075	0.40	5.45
	0.02500	0.00075	0.40	5.55
			Average	... 5.29
50°C	0.00125	0.00075	0.40	6.30
	0.01875	0.00075	0.40	6.98
	0.02500	0.00075	0.40	7.18
			Average	... 6.82
70°C	0.01250	0.00075	0.40	7.82
	0.01875	0.00075	0.40	8.08
	0.02500	0.00075	0.40	8.20
			Average	... 8.03
98°C	0.01515	0.00116	0.40	8.68
	0.02020	0.00116	0.40	9.40
	0.02525	0.00116	0.40	9.39
			Average	... 9.16

It is clear from the above results that at different temperatures the equivalent of one mole of glycerol varies with temperature. In no case, however, complete oxidation of glycerol is possible for this will require 14 equivalents of ceric salt.

The kinetics of the oxidation of glycerol solution was studied at 30°, 40° and 50°C. The reactions were carried out in a Townson Mercer thermostat at the required temperature within a variation of $\pm 0.1^\circ\text{C}$. Measured volume of glycerol kept in the thermostat was added to ceric sulphate solution. The total volume was kept 100 ml. by diluting the stock glycerol solution. The rate of the loss of Ce⁺⁴ was estimated by taking out 5 ml. of the reaction mixture at definite intervals of time and quenching it in 5 ml. of ferrous ammonium sulphate solution, and finally titrating excess of the ferrous salt against a standard ceric sulphate solution using N-phenylanthranilic acid as internal indicator. The con-

centrations of ferrous salt and titrating ceric sulphate solution were kept to be the same as that of the overall concentration of ceric sulphate in the reaction mixture. Thus, the used ceric sulphate is the direct measure of the ceric sulphate used in the mixture taken out. Results are recorded in table 2 below.

TABLE 2

[Ceric sulphate]	=	0.01010M	=	0.01010N
[Glycerol]	=	0.2908M	=	1.02070N
[Sulphuric acid]	=	0.40N		
Temperature	=	30°C		

Time in minutes	Volume taken each time in ml.	Volume of Ce^{+4} 0.0101M consumed in ml.	$K_1 = \frac{2.303}{t} \log \frac{a}{(a-x)}$
10	5.0	0.48	0.01011
20	„	0.90	0.00993
30	„	1.24	0.00951
40	„	1.68	0.01023
50	„	1.98	0.01009
60	„	2.25	0.00997
70	„	2.54	0.01014
80	„	2.84	0.01048
90	„	3.46	0.01036
100	„	3.56	0.01057
Average value of $K_1 = 0.01014$			

K_1 is pseudo first order constant and K_2 or specific rate constant, is given by

$\frac{K_1}{0.2908 \times 3.51}$, where 3.51 is the average equivalent number for glycerol at 30°C.

Hence,

$$K_2 = 0.0096 \text{ litres gm. equiv}^{-1}.\text{min}^{-1}.$$

In table 3 the rate of the loss of Ce^{+4} in the presence of half the concentration of glycerol used in the previous table is recorded.

TABLE 3

[Ceric sulphate]	=	0.01010M	=	0.01010 N
[Glycerol]	=	0.1454M	=	0.51035 N
[Sulphuric acid]	=	0.40N		
Temperature	=	30°C		

Time in minutes	Volume taken from mixture in ml.	Volume of Ce^{+4} 0.0101M used in ml.	$K_1 = \frac{2.303}{t} \log \frac{a}{a-x}$
20	5.0	0.44	0.00461
40	„	0.90	0.00496
60	„	1.32	0.00510
80	„	1.72	0.00469
100	„	2.10	0.00545
120	„	2.34	0.00536
140	„	2.62	0.00530
160	„	2.94	0.00547
180	„	3.18	0.00561
Average K_1			= 0.005161

Therefore $K_2 = 0.01010$ litres gm. equi.⁻¹min.⁻¹.

results reported in tables 2 and 3, which are the mean of several experiments, From the it is clearly seen that the order of the reaction is of first order with respect to Ce^{+4} . The order n with respect to glycerine is given by the expression $\log K_1/K_2 = n \log 2$. The value of n is found to be unity. Thus the total order of the reaction is two.

Effect of Sulphuric acid Concentration

The rates of loss in a mixture of overall concentration of $\text{Ce}(\text{SO}_4)_2$ 0.0101 M and glycerol 0.2908 M in the presence of different concentrations of sulphuric acid were also investigated as described under tables 2 and 3. The first order constants obtained in the presence of different concentration of sulphuric acid and the values of K_2 specific rate constant are only recorded in table 4. In the last column the values of $K_2 \times \text{H}_2\text{SO}_4$ are also given.

TABLE 4

[Ceric sulphate]	=	0.01010M	=	0.01010 N
[Glycerol]	=	0.2908M	=	1.02070 N
Temperature	=	30°C		

Serial no.	Final conc. of H_2SO_4 (N)	1st order constant K_1	K_2 in litres gms. eq. ⁻¹ min ⁻¹ .	$K_2 \times [H_2SO_4]$
1	0.40	0.01029	0.01008	0.00403
2	0.60	0.00781	0.00765	0.00459
3	0.80	0.00571	0.00559	0.00447
4	1.00	0.00584	0.00572	0.00572
5	1.60	0.00363	0.00356	0.00569
6	3.20	0.00147	0.00144	0.00451

Thus increasing concentration of sulphuric acid decreases the specific rate constant but the values of $K_2 \times [H_2SO_4]$ are constant within reasonable limits. Hence

$$K_2 \propto \frac{1}{[H_2SO_4]}$$

Effect of Temperature : The effect of temperature was also investigated and the summary of the results obtained is noted below :

TABLE 5

[Ceric sulphate]	=	0.01010 M
[Glycerol]	=	0.1454 M
$[H_2SO_4]$	=	0.4 N

Temperature in °C	K_1	K_2
30	0.03548	0.01011
40	0.13380	0.02530
50	0.64680	0.09480

In the second column the first order rate constants K_1 are given, whilst in the last column the values of K_2 are given, which have been calculated by taking into account the equivalents of Ce^{+4} required to oxidise one mole of glycerol at different temperatures (*vide* table 1)

Temperature Coefficient and Heat of Activation :

The temperature coefficients for this reaction are calculated for 10°C rise and are noted in table 6.

TABLE 6

Between 30° and 40°C	Between 40° and 50°C	Between 30° and 50°
2.51	3.74	4.69
3.78	4.83	7.70

Energy of Activation :

The energy of activation of this reaction is calculated from the relation

$$\log \frac{K_{T_2}}{K_{T_1}} = \frac{E}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

The values of heat of activation calculated from the values of the first order constants K_1 and specific rate constants K_2 obtained at different temperatures are noted as E_1 and E_2 respectively, in the following table :

TABLE 7

E_2	17.32 K. Cals.	26.53 K. Cals.	21.78 K. Cals.
E_1	25.03 K. Cals.	31.64 K. Cals.	28.24 K. Cals.

The results obtained here show that the heats of activation calculated from the rate constants K_1 are unusually high for a bimolecular change. This is, however, not so magnified when these values are calculated from the values of K_2 or specific rate constants at different temperatures.

SUMMARY AND CONCLUSION

The results obtained here show that,

- (i) The reaction between Ce^{+4} and glycerol in aqueous solution is of the second order.
- (ii) Increasing concentration of sulphuric acid decreases the velocity of chemical change and the rate constant is found to be inversely proportional to sulphuric acid concentration. This supports the observations of earlier workers that the formation of a complex takes place with sulphuric acid resulting to the removal of Ce^{+4} ions from the system



- (iii) The temperature coefficient of the reaction is unusually high and the heat of activation increases with increasing temperature,

This may be ascribed to the oxidation of glycerol to different extents at different temperatures. Further work is necessary in order to elucidate the mechanism of oxidation of glycerol at different temperatures by the oxidant Ce^{+4} .

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DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS BY HYDROUS OXIDES

PART I: HYDROUS Zr(IV) OXIDE

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[Received on 26th February, 1962]

ABSTRACT

In this paper the decomposition of hydrogen peroxide in the presence of Zr(IV) oxide is described. The results obtained indicate that the first order constants are fairly constant where higher concentration of the peroxide are used but they tend to decrease with the progress of reaction specially for the dilute solutions of hydrogen peroxide. It has also been observed that the loss of hydrogen peroxide as estimated by permanganate is very fast in the early stages of the reaction. The catalytic behaviour of hydrous Zr(IV) oxide towards the decomposition of the peroxide as noted here can be explained on the view that a true peroxy compound and also an unstable compound of the type $(OH)_2Zr-O-OH$ are formed on the surface of the hydrous oxide. The latter yields OH radical which initiates the cyclic decomposition of hydrogen peroxide.

INTRODUCTION

Hydrogen peroxide is known to decompose in the presence of several hydrous oxides as those of iron (III)¹⁻⁴, Cu(II)^{5,6}, Mn (IV)⁷ Co(III)⁸ etc. A detailed study of decomposition of the peroxide in the presence of hydrous nickel oxide⁹ has been reported from these laboratories.

EXPERIMENTAL

Zr(IV) hydrous oxide was prepared by the addition of an excess aqueous ammonia to a concentrated solution of zirconium nitrate in a moderately strong solution of hydrochloric acid. The gelatinous precipitate so obtained was washed free from nitrate and chloride ions and was stored in a jena bottle in contact with water. 10 ml of this suspension were found to contain 0.0647 gm of zirconium oxide and the supernatant liquid had a pH of 9.

The decomposition of hydrogen peroxide was studied with one month aged sample of hydrous Zr(IV) oxide. The freshly prepared one catalysed the decomposition so fast that it was impossible to follow the rate.

90 ml of the solution of hydrogen peroxide of known concentration were taken in a conical flask and kept in a thermostat. The jena bottle containing the suspension of the hydrous oxide was also kept in the same thermostat to attain the desired temperature. This was well shaken and 10 ml of the suspension were drawn from the container and were added to the conical flask. 10 ml of the mixture in the conical flask were drawn out at different intervals of time after shaking it well. The reaction was checked with 10—15 ml of 4N sulphuric acid, and the hydrogen peroxide was estimated by a potassium permanganate solution of a strength, which was double the concentration of hydrogen peroxide originally present in the conical flask.

In the following tables, first order constants calculated with the initial concentration of hydrogen peroxide are given in column 3. In column 4 the first order constants calculated with the concentration of the peroxide left after its quick loss in the initial stage of the reaction are given.

Temperature = 30°C.

Table 1

Final conc. of $H_2O_2 = 0.05M$

Time (mins.)	KMnO ₄ (ml.)	First order constants $K/2.303$	First order constants after initial fall
0	5.00	---	---
5	4.30	0.0131	---
10	4.05	0.0091	---
20	3.60	0.0071	---
30	3.20	0.0064	0.0051
40	2.90	0.0059	0.0046
50	2.60	0.0056	0.0047
60	2.30	0.0056	0.0048
80	1.90	0.0052	0.0046

Table 2

Final Conc. of $H_2O_2 = 0.025N$

Time (mins.)	KMnO ₄ (ml.)	First order constants $K/2.303$	First order constants after initial fall
0	5.00	---	---
5	3.90	0.0215	---
10	3.40	0.0167	---
15	3.10	0.0138	---
20	2.80	0.0125	---
30	2.30	0.0112	0.0085
40	1.95	0.0102	0.0078
50	1.65	0.0096	0.0076
60	1.40	0.0092	0.0075

Temperature = 30°C

Table 3

Final conc. of $H_2O_2 = 0.0125N$

Time (mins.)	KMnO ₄ (ml.)	First order constants $K/2.303$	First order constants after initial fall
0	5.00	---	---
5	3.30	0.0361	---
10	2.80	0.0251	---
15	2.40	0.0212	---
20	2.10	0.0188	---
30	1.60	0.0164	0.0118
40	1.30	0.0146	0.0104
50	1.15	0.0127	0.0087
60	1.00	0.0116	0.0080

Table 4

Final conc. of $H_2O_2 = 0.005N$

Time in (mins.)	KMnO ₄ (ml.)	First order constants $K/2.303$	First order constants after initial fall
0	5.00	---	---
5	2.80	0.0503	---
10	2.30	0.0337	---
15	2.00	0.0265	0.0121
20	1.70	0.0234	0.0131
25	1.50	0.0209	0.0123
30	1.40	0.0184	0.0107
50	1.30	0.0117	0.0061

Effects of several neutral salts viz., KCl , K_2SO_4 , BaCl_2 , etc. were also investigated. It was found that these salts have hardly any appreciable effect on the reaction velocity, but potassium fluoride considerably depressed the decomposition rate as noted in the tables below :

Temperature = 35°C

Table 5

Final conc. of $\text{H}_2\text{O}_2 = 0.0125\text{N}$
 Conc. of $\text{KF} = 0.05\text{N}$
 $\text{H}_2\text{O}_2 + \text{H}_2\text{O} + \text{KF} + \text{Sus}$
 50 ml. + 36 ml. + 4 ml. + 10 ml.

Time (mins.)	KMnO_4 (ml.)	First order constants $K/2.303$
0	5.00	---
5	4.40	0.0111
10	4.00	0.0096
15	3.70	0.0087
20	3.40	0.0083
30	3.10	0.0069
50	2.60	0.0056
80	2.10	0.0047

Table 6

Final conc. of $\text{H}_2\text{O}_2 = 0.0125\text{N}$
 $\text{H}_2\text{O}_2 + \text{H}_2\text{O} + \text{Sus}$
 50 ml. + 40 ml. + 10 ml.

Time (mins.)	KMnO_4 (ml.)	First order constants $K/2.303$
0	5.00	---
5	3.20	0.0387
10	2.60	0.0284
15	2.10	0.0251
20	1.70	0.0234
30	1.30	0.0195
50	1.00	0.0148

A sample of the hydrous oxide was kept in contact with a moderately strong hydrogen peroxide solution. When all the hydrogen peroxide decomposed, the hydrous oxide thus left over was used for the decomposition of hydrogen peroxide solutions and the result is given in table 7.

Temperature = 35°C .

Table 7

Final conc. of $\text{H}_2\text{O}_2 = 0.025\text{N}$

Time in (mins.)	KMnO_4 (ml.)	First order constants $K/2.303$
0	5.00	---
5	4.70	0.0053
10	4.20	0.0075
20	3.50	0.0077
30	3.00	0.0073
40	2.50	0.0075
50	2.10	0.0075
60	1.80	0.0073

Table 8

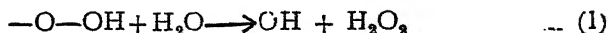
Time (mins.)	KMnO_4 (ml.)	First order constants $K/2.303$	First order constants after initial fall.
0	5.00	---	---
5	3.85	0.0227	---
10	3.40	0.0167	---
15	2.90	0.0157	---
20	2.55	0.0146	---
30	2.10	0.0125	0.0084
40	1.70	0.0117	0.0088
50	1.40	0.0110	0.0086
60	1.20	0.0103	0.0081

It is seen from the tables 1—4 that the loss of hydrogen peroxide as estimated with potassium permanganate is very fast in the earlier stages of the reaction and this increases with the decreasing concentrations of the peroxide. The first order constants calculated with the initial concentrations of hydrogen peroxide decrease with the progress of the reaction, but those calculated with the concentration of the peroxide left after a quick fall in its concentration are in fair agreement for the higher concentrations of hydrogen peroxide. These, however, tend to decrease with the increasing dilutions of the peroxide suggesting that the order of decomposition increases. It will be also seen from table 7 that previously treated hydrous Zr(IV) oxide with hydrogen peroxide also decomposes hydrogen peroxide, but there is no quick fall in the concentration of the peroxide in the initial stages and that the rate of decomposition is also comparatively slow. The first order constants are fairly constant and the reaction follows the unimolecular law.

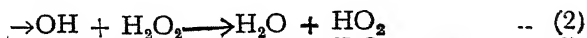
Considerable effect in decreasing the rate of decomposition of hydrogen peroxide is seen in the case of potassium fluoride in presence of Zr(IV) hydrous oxide (*vide* tables 5—6). The loss of hydrogen peroxide is very slow when higher concentrations of potassium fluoride are used but it increases with the decreasing concentrations of potassium fluoride. This is ascribed to the capacity of fluoride anion to form coordination compound with zirconium. Thus the surface activity of hydrous Zr(IV) oxide for the decomposition of hydrogen peroxide is considerably decreased.

DISCUSSION

Like the peroxide of rare earth Ce^{+4} , zirconium is also known to yield peroxide and hydrous Zr(IV) oxide is known to form $ZrO_3 \cdot 2H_2O$. The hydrated peroxy zirconic acid $H_2ZrO_4 \cdot H_2O$ in its formation by the action of hydrogen peroxide on hydrous Zr(IV) oxide first yields an adsorption complex. Thus it may be passing through an unstable state of peroxy compound and finally to a true peroxy compound with the prolonged time of interaction. It is well known that a stable peroxy compound such as potassium persulphate yields iodine from potassium iodide at pH 7.5 but no oxygen is evolved. On the other hand, a compound containing hydrogen peroxide of crystallisation and specially an unstable peroxy compound is easily hydrolysed to form hydrogen peroxide. Thus the group $-O-OH$ of $(OH)_3Zr-O-OH$ undergoes hydrolysis as:



The generation of OH thus leads to the cyclic decomposition of hydrogen peroxide as suggested by Haber and Willstätter¹⁰:



It has been noted that hydrous Zr(IV) oxide after treatment with hydrogen peroxide yields a product which liberates iodine in neutral medium and also consumes some permanganate in acid medium. This leads to the conclusion that the so called peroxide of zirconium yields a true peroxy compound and also an unstable peroxy compound by the treatment of hydrogen peroxide with hydrous Zr(IV) oxide. As the order of decomposition tends to increase from one to two, it may be concluded that either one of the two reactions (2 and 3) is slow and determines the rate of decomposition.

Obviously the formation of the percompounds by the interaction of hydrous oxide and hydrogen peroxide is preceded by the phenomenon of adsorption, which becomes independent of the concentration of hydrogen peroxide where higher concentrations of the peroxide are used. It is for this reason that the order of decomposition tends to increase with the lower concentrations of hydrogen peroxide.

The authors acknowledge with thanks the research grant received from the Scientific Research Committee, U. P. which has made the investigations made here possible.

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DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS BY HYDROUS OXIDES

PART II : HYDROUS COBALT (III) OXIDE

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[Received on 26th February, 1962]

ABSTRACT

This paper deals with the decomposition of hydrogen peroxide in presence of hydrous Co (III) oxide. The experiments show that the rate of the loss of hydrogen peroxide is of first order except at lower concentrations of the peroxide where it tends to be of second order. The order of decomposition is also found to increase with the rise of temperature. The decomposition of hydrogen peroxide on the surface of hydrous Co (III) oxide is supposed to involve a reduction-oxidation cycle as has been suggested for the catalytic action of manganese dioxide.

INTRODUCTION

In Part I of this series¹ the catalytic effect of hydrous Zr (IV) oxide in the decomposition of hydrogen peroxide, has been described. As early as 1879 Bayley observed that during the precipitation of Co (II) oxide from a cobaltous salt solution by the addition of an alkali in the presence of the peroxide oxygen was evolved. Similarly, Tryhorn and Jessop² and also Broughton, Wentworth and Farnsworth³ have reported that hydrogen peroxide decomposes in the presence of hydrous Co (III) oxide when formed by the oxidation of hydrous cobaltous oxide in the presence of hydrogen peroxide. Thus the catalytic effect of hydrous Co (III) oxide is well recognised but this is not yet fully investigated.

EXPERIMENTAL

A concentrated solution of cobaltous chloride was prepared and to this normal caustic soda solution was added gradually when a lavender coloured gel of cobaltous hydroxide was obtained which changed to green and finally to a deep blue gel on further addition of caustic soda. The deep blue gel was oxidised to black hydrous cobaltic oxide by the action of alkaline bromine. This black oxide was washed free from chloride, bromide and OH⁻ ions and was stored in a jena bottle in contact with water. 5 ml. of suspension were found to contain 0.0408 gm. of cobaltic oxide and the pH of the suspension was 6.2.

The conical flask containing 95 ml of hydrogen peroxide solution of known concentration and the hydrous oxide bottle were kept in a precision thermostat to attain the required temperature. 5 ml of the hydrous oxide suspension were drawn from the container after shaking it well and were added to the conical flask. 10 ml of the contents of the flask were sucked out at different intervals of time and were added to the test tubes containing 5 ml of 4 N sulphuric acid solution to check the reaction. The tubes were centrifuged and 5 ml of the supernatant liquid were estimated for hydrogen peroxide against a standard permanganate solution.

The results are recorded in the following tables :

Temperature = 30°C

Table 1

Final conc. of H_2O_2
= 0.10 N

Time in mins.	KMnO_4 ml.	First order constants $K/2.303$
0	5.00	---
5	4.70	0.0053
15	4.30	0.0043
30	3.90	0.0035
45	3.50	0.0034
60	3.10	0.0034
75	2.80	0.0033
90	2.50	0.0033
105	2.30	0.0032
120	2.00	0.0033

Table 2

Final conc. of H_2O_2
= 0.05 N

Time in mins.	KMnO_4 ml.	First order constants $K/2.303$
0	5.00	---
15	4.20	0.0050
30	3.80	0.0039
45	3.00	0.0049
60	2.70	0.0044
75	2.30	0.0044
90	2.00	0.0044
105	1.75	0.0043
120	1.60	0.0041

Table 3

Final conc. of H_2O_2
= 0.025 N

Time in mins.	KMnO_4 ml.	First order constants $K/2.303$
0	5.00	---
15	3.80	0.0079
30	3.05	0.0071
45	2.45	0.0068
60	1.90	0.0070
75	1.60	0.0066
90	1.30	0.0065
105	1.00	0.0066
120	0.70	0.0071

Table 4

Final conc. of H_2O_2
= 0.0125 N

Time in mins	KMnO_4 ml.	First order constants $K/2.303$
0	5.00	---
5	3.10	0.0415
10	2.55	0.0292
15	2.05	0.0258
20	1.45	0.0268
30	1.20	0.0206
40	0.90	0.0186
50	0.80	0.0159

Temperature = 35°C
Table 5

Time in mins.	KMnO ₄ ml.	First order constants $K/2.303$
0	5.00	---
5	4.60	0.0072
15	4.10	0.0050
30	3.60	0.0047
45	3.10	0.0046
60	2.60	0.0047
75	2.25	0.0046
90	1.90	0.0046
105	1.70	0.0044
120	1.45	0.0044

Final conc. of H₂O₂ = 0.10 N
Temp. = 40°C
Table 6

Time in mins.	KMnO ₄ ml.	First order constants $K/2.303$
0	5.00	---
5	4.40	0.0111
15	3.80	0.0079
30	3.20	0.0064
45	2.60	0.0063
60	2.20	0.0059
75	1.90	0.0056
90	1.60	0.0055
105	1.30	0.0055
120	1.10	0.0054

It is seen from tables 1—4 that the order of decomposition of hydrogen peroxide in the presence of hydrous Co (III) oxide the first order constants tend to decrease with time, but this behaviour becomes very prominent for the dilute solutions of the peroxide (*vide* table 4). This shows that for dilute solutions of the peroxide the order of the decomposition tends to increase.

The effect of neutral salts *viz.*, KCl, BaCl₂, K₂SO₄ and KF on the decomposition of hydrogen peroxide in the presence of hydrous Co (III) oxide has also been investigated but no appreciable effect has been observed.

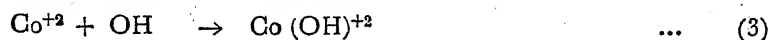
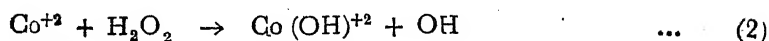
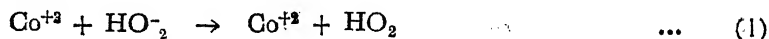
Table 7 gives the temperature coefficient, energy of activation E , frequency factor A and the entropy of activation ΔS at 30°C.

Table 7

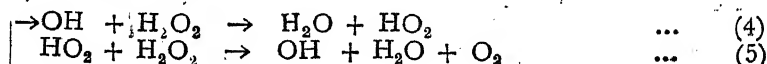
Temperature range	Temperature coefficient	E in cal.	Average A encounters per minute $A \times 10^{-2}$	ΔS in c. u.
30° – 35°C	1.33	---	9.926	-52.99
35° – 40°C	1.11	---	---	---
30° – 40°C	1.48	7506	---	---

DISCUSSION

The results of the preceding experiments on the decomposition of hydrogen peroxide in the presence of hydrous Co (III) oxide indicate that the reaction is of first order when stronger solutions of hydrogen peroxide are used, but it tends to be of higher order when very dilute solutions of the peroxide are employed. Cobaltic oxide is an oxidised product of cobaltous oxide and can be obtained by the oxidation of the latter by hydrogen peroxide. We may, therefore, conclude that further oxidation of the hydrous Co (III) oxide is not possible. Hence the mechanism of the catalytic action of this hydrous oxide for hydrogen peroxide appears to be different from that reported for the hydrous Zr(IV) oxide¹. We are of the opinion that the chain of reactions leading to the catalytic decomposition of hydrogen peroxide noted here is initiated by the reducing property of hydrogen peroxide as has been suggested for the catalytic action of manganese dioxide. Chain of reactions is as noted below :



Reaction (3) is a chain breaking step. The radicals OH or HO₂ initiate the cyclic decomposition of hydrogen peroxide according to the scheme suggested by Haber and Willstätter (*vide*.¹)



The dissociation of hydrogen peroxide as an acid yields HO₂⁻ which acts as a reducing species present in hydrogen peroxide.

It is significant to observe here that the study of Broughton, Wentworth and Farnsworth³ using radioactive tracers technique could not support the mechanism of catalytic decomposition of hydrogen peroxide in the presence of Co⁺³ as similar to that in the presence of manganese dioxide. We are, however, of the opinion that the oxidation-reduction potential of Co⁺³ being one of the highest, its further oxidation to, still higher state does not seem possible.

The first step or the reduction of Co⁺³ to Co⁺² is preceded by the adsorption of hydrogen peroxide and subsequent oxidation of Co⁺² to Co⁺³ occurs on the surface. Hence for higher concentrations of hydrogen peroxide the amount adsorbed shall be independent of the concentration of hydrogen peroxide and therefore the rate of decomposition should tend towards zero order which is not an experimental fact. If we assume that one of the steps in the chain process is rate determining one, the reaction shall be of first order for higher concentrations of hydrogen peroxide, but with increasing dilutions of the peroxide the reaction will tend to become of second order.

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ON RICE'S POLYNOMIALS, $H_n(\xi, p, v)$

By

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[Received on 7th February, 1959]

1. *Introductory.* Rice (1940) has introduced the polynomial

$$H_n(\xi, p, v) = {}_2F_1 \left[\begin{matrix} -n, n+1 \\ 1 \end{matrix} ; \xi; v \right], \quad (1.1)$$

where $n=0, 1, 2, \dots$, and ξ, p, v are complex variables, but $p \neq -n-1, -n-2, \dots$. He further found that

$$H_n(\xi, p, v) = \frac{\Gamma(p)}{\Gamma(\xi) \Gamma(p-\xi)} \int_0^1 t^{\xi-1} (1-t)^{p-\xi-1} P_n(1-vt) dt, \quad (1.2)$$

where $\text{Re } p > \text{Re } \xi > 0$, and $P_n(z)$ is the Legendre polynomial.

In an attempt to unify and to extend the study of certain sets of polynomials, Fassenmyer (1947) gave the Generalised Hypergeometric polynomials.

$$\begin{aligned} f_n(a_i; b_i; x) &= f_n(a_1, \dots, a_p; b_1, \dots, b_q; x) \\ &= {}_{p+2}F_q \left[\begin{matrix} -n, n+1 \\ 1/2, 1 \end{matrix} ; a_1, \dots, a_p; b_1, \dots, b_q; x \right] \end{aligned} \quad (1.3)$$

$$H_n(\xi, p, v) \text{ is a special case of } f_n(a_i; b_i; x) \quad (1.4)$$

$$H_n(\xi, p, v) = f_n(1/2, \xi; p; v)$$

The object of this paper is to obtain some results involving Rice's polynomials. The results are believed to be new.

Throughout this paper the integration has been used in the sense of Riemann.

2. *Series involving $H_n(\xi, p, v)$.*

Since [3]

$$z^n = \sum_{s=0}^{[n/2]} \frac{(2n-4s+1) n! \Gamma(1/2)}{2^{n+1} s! \Gamma(n-s+1/2)} P_{n-2s}(z) \quad (2.1)$$

where z is a complex variable, and

$$\int_0^1 t^{\xi-1} (1-t)^{p-\xi-1} (1-2vt)^n dt \quad (2.2)$$

$$= \frac{\Gamma(p-\xi) \Gamma(\xi)}{\Gamma(p)} {}_2F_1 \left[\begin{matrix} -n, \xi \\ p \end{matrix}; 2v \right];$$

$$\operatorname{Re} p > \operatorname{Re} \xi > 0;$$

Therefore in (2.1) putting $z = 1 - 2vt$, multiplying the two sides by $t^{\xi-1}$ $(1-t)^{p-\xi-1}$ and integrating between the limits 0 and 1, we get

$${}_2F_1 \left[\begin{matrix} -n, \xi \\ p \end{matrix}; 2v \right] = \sum_{s=0}^{[n]} \frac{(2n-4s+1) n! \Gamma(1/2)}{2^{n+1} s! \Gamma(n-s+3/2)} H_{n+2s}(\xi, p, v), \quad (2.3)$$

where $\operatorname{Re} p > \operatorname{Re} \xi > 0$.

We have [1, vol. 2, p. 294]

$$(1-x)^\rho = 2^\rho \sum_{n=0}^{\infty} \frac{(2n+1) (-\rho)_n}{(n+\rho+1) (1+\rho)_n} P_n(x) \quad (2.4)$$

which is absolutely convergent when $\rho > -3/4$ and

$-1 \leq x \leq 1$. Set $x = 1 - 2vt$, then

$$(vt)^\rho = \sum_{n=0}^{\infty} \frac{(2n+1) (-\rho)_n}{(n+\rho+1) (1+\rho)_n} P_n(1-2vt) \quad (2.5)$$

and therefore provided $|1-2v| \leq 1$

$$v^\rho = \frac{\Gamma(\xi) \Gamma(p+\rho)}{\Gamma(p) \Gamma(p+\xi)} \sum_{n=0}^{\infty} \frac{(2n+1) (-\rho)_n}{(n+\rho+1) (1+\rho)_n} H_n(\xi, p, v) \quad (2.6)$$

where $\operatorname{Re} p > \operatorname{Re} \xi > 0$, $\operatorname{Re}(\rho+\xi) > 0$ and $\rho > -3/4$.

The series in the relation [4, p. 365]

$$z^{1/2} e^{z\xi} = \sqrt{\frac{1}{2}\pi} \sum_{n=0}^{\infty} (2n+1) P_n(\xi) I_{n+1/2}(z) \quad (2.7)$$

is absolutely convergent for all finite values of z , when $-1 \leq \xi \leq 1$.

Therefore we obtain

$$\begin{aligned} & z^{1/2} e^{z\xi} {}_1F_1 \left[\begin{matrix} \xi \\ p \end{matrix}; -2v \right] \\ &= \sqrt{\frac{1}{2}\pi} \sum_{n=0}^{\infty} (2n+1) I_{n+1/2}(z) H_n(\xi, p, v) \end{aligned} \quad (2.8)$$

where $\operatorname{Re} p > \operatorname{Re} \xi > 0$ and $|1-2v| \leq 1$

3. A recurrence formula for $H_n(\xi, p, v)$

From the recurrence formula [4, p. 99]

$$(n+1) P_{n+1}(\mu) - (2n+1) \mu P_n(\mu) + n P_{n-1}(\mu) = 0$$

we easily obtain the recurrence relation

$$(n+1) H_{n+1}(\xi, p, v) - (2n+1) H_n(\xi, p, v) + \frac{2v\xi}{p} (2n+1) H_n(\xi+1, p+1, v) + n H_{n-1}(\xi, p, v) = 0,$$

where $\text{Re } p > \text{Re } \xi > 0$.

4. Application of Shastri's theorem.

Shastri [6, p. 215] has given the following theorem.

$$\text{If } f(p) = p \int_0^\infty e^{-px} h(x) dx$$

$$\text{and } 1/p^s h(1/p) = p \int_0^\infty e^{-px} g(x) dx$$

$$\text{then } f(p) = 2 p^{s/2+1} \int_0^\infty t^{-s/2} g(t) K_s(2\sqrt{pt}) dt$$

provided $\text{Re } p > 0$; $g(t)$ is bounded and integrable in the right-open interval $(0, \infty)$, and

$$\int_0^\infty |g(t)| dt$$

is convergent, K_s represents Bessel function of the second kind.

We have [1, vol. I, p. 215]

$$Z_n(z) = {}_2F_2 \left[\begin{matrix} -n, n+1 \\ 1, 1 \end{matrix}; z \right]$$

a polynomial given by Bateman.

This gives

$$p \int_0^\infty e^{-pz} Z_n(z) z^{\xi-1} dz = \frac{\Gamma(\xi)}{p^{\xi-1}} H_n(\xi, 1, 1/p)$$

where $\operatorname{Re} p > 0$ and $\operatorname{Re} \xi > 0$.

Using Shastri's theorem we get

$$\begin{aligned} & {}_4F_2 \left[\begin{matrix} -n, n+1, \xi, \xi-s \\ 1, 1 \end{matrix}; 1/p \right] \\ &= \frac{2 p^{\xi-s/2}}{\Gamma(\xi) \Gamma(\xi-s)} \int_0^\infty t^{\xi-s/2-1} Z_n(t) K_n(2\sqrt{pt}) dt \end{aligned} \quad (4.4)$$

where $\operatorname{Re} p > 0$ and $\operatorname{Re} s > \operatorname{Re} \xi > 0$.

Using the same theorem we shall get

$$\begin{aligned} & H_n(\xi, 1, 1/p) \\ &= \frac{2 p^{\xi+s/2}}{\Gamma(\xi) \Gamma(\xi+s)} \int_0^\infty t^{\xi+s/2-1} {}_2F_2 \left[\begin{matrix} -n, n+1 \\ 1, 1, \xi+s \end{matrix}; t \right] K_n(2\sqrt{pt}) dt \end{aligned} \quad (4.5)$$

where $\operatorname{Re}(\xi+s) > 0$, $\operatorname{Re} \xi > 0$ and $\operatorname{Re} p > 0$.

My thanks are due to the Late Dr. N. G. Shabde for the help and guidance he gave to me during the preparation of this paper. I am also thankful to the referee for his various useful suggestions.

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CHEMICAL EXAMINATION OF TRIFOLIUM INDICUM, LINN. PART I

EXAMINATION OF THE FATTY OIL FROM THE SEEDS

By

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[Received on 27th March, 1961]

Trifolium Indicum, Linn. commonly known as Vana-methi belongs to *Papilionaceae* sub-group of *Leguminosae* family and grows wildy in Western Peninsula, Bengal and Uttar Pradesh. The seeds are astringent and are claimed to be useful in colic, diarrhoea and other bowel complaints. They are also used in dysmenorrhoea and rheumatism and as a blood purifier.¹ In view of its medicinal properties, a systematic chemical examination of *Trifolium Indicum*, Linn. has therefore been undertaken and the present communication deals with the examination of the fatty oil obtained from the seeds.

EXPERIMENTAL

The fatty oil was obtained in 8.8% yield by extracting the powdered seeds (2 Kg.) with petroleum ether (b. p. 40°—60°) and evaporation of the solvent. It was bright yellow in colour. The oil was purified by repeated treatment with animal charcoal and Fuller's earth. It was non-drying and possessed the following characteristics :

Specific gravity at 30°	0.928
Refractive index at 30°	1.465
Acid value	11.400
Acetyl value	18.250
Saponification value	196.860
Iodine value (Hanus)	111.750
R. M. value	0.310
Hehner number	92.640
Thiocyanogen value	86.800
Unsaponifiable matter %	1.620

Examination of fatty acids : The oil (50 g.) was saponified in the usual manner, the unsaponifiable matter extracted with ether and the fatty acids were liberated by treatment of the soap with dilute sulphuric acid. The mixed acids possessed the following properties :

Molecular Weight	278.6
Iodine value	118.2

'The mixed acids were separated into saturated and unsaturated acids by Twitchell' lead salt alcohol method, modified by Hilditch². The liberated acids possessed the following properties :

TABLE 1
Characteristics of the liberated acids

Serial No.	Acids	% yield	Iodine value	Thio-cyanogen value	Neutral value	Mean Mol. Weight.
1.	Mixed acids	—	118.2	86.8	182.5	278.6
2.	Solid acids	22.12	3.3	2.6	183.2	364.5
3.	Liquid acids	77.88	130.8	88.2	184.6	286.2

The liquid and solid acids were converted into their methyl esters and the mixed esters were fractionally distilled under reduced pressure. The loss in distillation was made good by adding proportionately to each fraction. The saponification value, iodine value and mean Molecular Weight of each fraction was determined and the composition of the esters was calculated in the usual manner.

TABLE 2
Liquid esters distilled at 10 mm.

Serial No.	Weight in g.	Temp. in °C.	I. V.	S. V.	Mean M. W.	Methyl esters in g.			
						Palmi-tate.	Lino-lenate	Lino-leate.	Ole-ate
1	4.1	185-195	134.0	201.3	280.2	2.00	2.10	—	—
2	6.8	195-205	243.4	192.2	292.6	0.28	5.36	1.16	—
3	13.5	205-210	198.5	191.5	292.4	—	3.85	9.65	—
4	11.3	210-215	153.4	190.6	295.0	—	—	8.86	2.44
5	17.0	215-220	138.2	190.0	294.6	—	—	10.40	6.60
6	29.4	220-230	128.6	190.0	294.6	—	—	14.25	15.15
7	9.0	230-240	116.5	189.4	295.2	—	—	3.30	5.70
8	8.9	Residue	98.0	188.8	296.0	—	—	1.12	7.78
Total	100.0					2.28	11.31	48.74	37.67

TABLE 3
Solid esters distilled at 5 mm.

Serial No.	Weight in g.	Temp. in °C.	I.V.	S.V.	Mean M.W.	Methyl esters in g.		
						Erucate	Palmitate	Stearate
F. 1	6.16	215-220	31.2	186.4	300.0	2.60	3.33	0.23
F. 2	9.84	220-225	34.5	183.4	305.4	4.77	4.70	0.37
F. 3	7.50	225-230	43.0	178.8	314.5	4.40	2.60	0.50
F. 4	6.65	230-240	54.0	170.0	330.2	5.05	1.10	0.50
F. 5	5.00	240-250	60.2	166.5	337.5	4.15	0.10	0.75
F. 6	7.22	250-260	56.6	166.0	337.2	5.65	0.17	1.40
F. 7	7.63	Residue	53.4	166.0	335.6	5.43	0.20	2.00
Total	50.00					32.05	12.20	5.75

Identification of the acids : The above fractions of the methyl esters were separately treated with urea in methyl alcohol and the fractionation of urea-adduct was carried out by the procedure adopted by Mehta and Abhyankar³. The liberated esters from urea adducts were hydrolysed and the liberated acids were identified in the usual manner.

Identification of the liquid acids : The liquid acids from fractions 1, 3 and were oxidised with dilute potassium permanganate solution according to the method of Lapworth and Mottram⁴, when a hexahydroxy-stearic acid (m.p. 203°) was obtained from Fraction 1, and dihydroxy-stearic acid (m.p. 130°) was obtained from Fractions 3 and 7. A small amount of the residue was left unoxidised in Fraction 1 and it was subsequently identified as palmitic acid (m.p. 62°).

The quantities of the liquid acids were also determined by bromination of the liquid acids in ethereal solution at -10° according to the method of Muggenthaler⁵ as modified by Jameison and Boughman⁶ when linolenic hexabromide (m.p. 178°-179°) and linolenic tetrabromide (m.p. 112°-113°) were obtained. The former was insoluble in ether while the latter was insoluble in petroleum ether (b.p. 40°-60°).

Identification of the solid acids : By treating the solid fractions F. 1 to F. 7 separately with alkaline potassium permanganate, dihydroxy-behenic acid (m.p. 129°) was obtained in each solid fraction. This indicated the presence of erucic acid in all the fractions. The un-oxidised residue left was resolved into palmitic and stearic acids. The presence of these acids were confirmed by determining the m.p. and mixed m.p. with authentic specimens of these acids when no depression in m.p. was observed.

CONCLUSIONS

On analysis, the fatty oil obtained from the seeds of *Trifolium Indicum*, Linn. was found to have the following composition :

Linolenic acid	...	7.55 percent.
Linoleic acid	...	32.50 percent.
Oleic acid	...	25.00 percent.
Erucic acid	...	21.50 percent.
Palmitic acid	...	9.65 percent.
Stearic acid	...	3.80 percent.

The un-saponifiable matter consists of sitosterol and a small proportion of yellow colouring matter.

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A NEW APPROACH TO SMOLUCHOWSKI'S EQUATION

By

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[Received on 16th November, 1961]

Zsigmondy¹ for the first time studied quantitatively the kinetics of coagulation. His experiments were theoretically developed by Smoluchowski² in the form of a well known equation. Smoluchowski's theory of coagulation was criticized by many authors, viz., Kruyt, and Van Arkel,³ Westgren and Reistötter⁴ and Ghosh.⁵ Fuch⁶ suggested an equation where the diffusion of particles was considered in a field of force instead of Smoluchowski's treatment by ordinary diffusion. Experimental support to this was given by Derjguin.⁷ Bhattacharya and his coworkers⁸ proposed an empirical equation inter-connecting concentration of added electrolyte and time of coagulation in the slow region. This equation has recently been justified by Ghosh and Gangopadhy⁹ on theoretical considerations.

Of the different factors, viz., deformation of the electrical double layer, dehydration, collision of almost uncharged particles etc., influencing the coagulation of colloidal solution, one factor, which appears to be of some significance to us, has not been considered by the different authors till now. It deals with the kinetic energy of the particles possessing residual charge. It appears quite probable that this energy may be quite sufficient to overcome the repelling action of charged particles thereby bringing about coalescence. Based on this assumption we have attempted to derive an equation which interestingly enough has taken the same form as the Smoluchowski's equation for slow coagulation.

Suppose only particles having an average critical energy ϵ are responsible for effective collision, when ϵ has got many degrees of freedom, then the probability P of the molecules having the average energy ϵ is given by¹⁰.

$$P = \frac{e^{-\epsilon/KT} (\epsilon/KT)^{S/2-1}}{(S/2-1)!} \text{ where } S \text{ is the degree of freedom,}$$

If n_0 is the number of molecules then $1/KT = 3n_0/\gamma E$

$$P = \frac{e^{-3\epsilon n_0/\gamma E} (3\epsilon n_0/\gamma E)^{S/2-1}}{(S/2-1)!}$$

Let Σn be the total number of molecules

$$P = \frac{e^{-3\epsilon \Sigma n/\gamma E} (3\epsilon \Sigma n/\gamma E)^{S/2-1}}{(S/2-1)!}$$

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Putting $3\epsilon/\gamma E = K$ and $(S/2 - 1) = B$

then

$$P = \frac{e^{-K\Sigma n} K^B \Sigma n^B}{|B|}$$

or

$$P = \frac{A e^{-K\Sigma n} \Sigma n^B}{|B|} \quad \text{where } A = K^B / |B|$$

For a single particle the number of collision is $8\pi RD (\Sigma n - n_1)$ where n_1 is the number of n doublets.

Since in our case only the particles having an excess average energy ϵ are responsible for collision and the probability for this is given by $A e^{-K\Sigma n} \Sigma n^B$. Hence total number of particles having the excess energy will be $\Sigma n A e^{-K\Sigma n} \Sigma n^B$.

Therefore the number of collision in Unit time will be

$$8\pi RD (\Sigma n A \Sigma n^B e^{-K\Sigma n} - n_1) n_1 = 8\pi RD (A \Sigma n^\gamma e^{-K\Sigma n} - n_1) n_1$$

where $\gamma = 1 + B$

Since $K < |B|$ the number of collision will be positive.

$$\text{Thus } dn_1 / dt = -8\pi RD n_1^2 - 8\pi RD (A \Sigma n^\gamma e^{-K\Sigma n} - n_1) n_1$$

$$\text{or } dn_1 / dt = -8\pi RD A \Sigma n^\gamma n_1 e^{-K\Sigma n}$$

the doublets will decrease at the rate of $8\pi RD A \Sigma n^\gamma n_2 e^{-K\Sigma n}$

$$dn_2 / dt = 8\pi RD (n_1^2/2 - n_2 A \Sigma n^\gamma e^{-K\Sigma n})$$

Similarly the triplets will decrease at the rate of

$$8\pi RD A \Sigma n^\gamma n_3 e^{-K\Sigma n}$$

$$dn_3 / dt = 8\pi RD (n_1 \cdot n_2 - A n_3 \Sigma n^\gamma e^{-K\Sigma n})$$

The solution of the differential equations is

$$nm = \frac{no (4\pi RD \text{ not})^{m-1}}{(1 + 4\pi RD A no^\gamma e^{-Kno})^{m+1}}$$

On further calculations

$$\Sigma n^{\gamma} e^{-K \Sigma n} = \frac{no^{\gamma} e^{-Kno}}{(1 + 4 \pi R D A no^{\gamma} e^{-Kno} t)}$$

Or $\Sigma n^{\gamma} e^{-K \Sigma n} = \frac{no^{\gamma}}{(1/e^{-Kno} + 4 \pi R D A no^{\gamma} t)}$

Or $\Sigma n^{\gamma} e^{K \Sigma n} = \frac{no^{\gamma}}{(e^{Kno} + 4 \pi R D A no^{\gamma} t)}$

Or $\Sigma n^{\gamma} / 1 + K \Sigma n = \frac{no^{\gamma}}{(1 + Kno + 4 \pi R D A no^{\gamma} t)}$

Since $1/\gamma < 1$

$$\frac{\Sigma n}{(1 + K \Sigma n)^{1/\gamma}} = \frac{no}{(1 + Kno + 4 \pi R D A no^{1/\gamma} t)^{1/\gamma}}$$

put $1/\gamma = b$ and expanding and neglecting higher powers being small.

$$\frac{\Sigma n}{1 + Kb \Sigma n} = \frac{no}{(1 + bKno + b 4 \pi R D A no^{1/b} t)}$$

put $b 4 \pi R D A no^{1/b} t = C$

$$\frac{\Sigma n}{1 + Kb \Sigma n} = \frac{no}{(1 + bKno + Ct)}$$

or $\frac{1 + Kb \Sigma n}{\Sigma n} = \frac{1 + bKno + Ct}{no}$

or $\frac{1}{\Sigma n} + Kb = \frac{1}{no} + bK \pm \frac{Ct}{no}$

or $\frac{1}{\Sigma n} = \frac{1}{no} + \frac{Ct}{no}$

or $\Sigma n = \frac{no}{1 + Ct}$

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ON UNIQUENESS OF SOLUTIONS OF A NON-LINEAR SYSTEM OF DIFFERENTIAL EQUATIONS

By

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[Received on 23rd January, 1962]

The purpose of this note is to establish by means of two lemmas a simpler Uniqueness Theorem for the solutions of the equation,

$$x' = f(t, x) \quad \dots \quad \dots \quad \dots \quad (1)$$

We also obtain an estimate, in the case of non-uniqueness, for the difference of two solutions of (1).

§ We consider the system of differential equations (1) where x denotes a n -dimensional Vector and $f(t, x)$ is a given Vector field which is defined in the Product space $\Delta = I \times R^n$ and is continuous there, where I is the interval $0 \leq t < \infty$ and R^n is the Euclidean space of n dimensions.

Let $V(t, U(t)) \geq 0$ be a scalar function also defined on Δ .

We assume that V satisfies a Lipschitz condition in U locally.

We define

$$V^*(t, U(t)) = \lim_{h \rightarrow 0+} \sup \frac{1}{h} [V(t+h, U) - V(t, U)]$$

The author has established the following lemma [I] in an earlier communication.

Lemma 1.

Let $W(t, r)$ be continuous on $I: 0 \leq t < \infty$,

$r \geq 0$. Suppose

$$V^*(t, U(t)) \leq W(t, V(t, U)) - \alpha V(t, U(t))$$

where $\alpha > 0$ is a suitably chosen number.

Further let

$$|f(t, x_1) - f(t, x_2)| \leq V(t, |x_1 - x_2|)$$

where $|x|$ indicates the Euclidean norm of x .

Let $r(t)$ be the maximal solution of $r' = w(t, r)$ with $r(t_0) \leq r_0$,
 $r_0 > 0$.

Then if $x_1(t)$ and $x_2(t)$ are any two solutions of (I),

$$\text{setting } U(t) = |x_1 - x_2|,$$

We have

$$V(t, U(t)) \leq r(t) \text{ for } t \geq t_0 \quad \dots \quad \dots \quad \dots \quad (2)$$

Lemma 2.

With the assumptions of lemma 1, if we further have

$$M(U) = \int_{U_0}^U [r(s)]^{-1} ds, \quad U_0 > 0 \quad \dots \quad \dots \quad \dots \quad (3)$$

Then we have

$$M(U(t)) \leq M(U(a_0 + \delta)) + t - (a_0 + \delta)$$

with $\delta > 0$, $a_0 + \delta < t$

Proof: We have

$$\begin{aligned} U(t) = |x_1 - x_2| &\leq \int_{a_0}^t |f(s, x_1(s)) - f(s, x_2(s))| ds \\ &\leq \int_{a_0}^t V(s, U(s)) ds \\ &= P(t) > 0 \text{ (say)} \\ &\text{for } t \geq a_0 \end{aligned}$$

Therefore

$$P'(t) = V(t, U(t))$$

From (2) and (3) we have

$$\frac{d}{dt} M(P(t)) \leq 1$$

integrating this between $(a_0 + \delta)$ and t we obtain

$$M(P(t)) \leq M(P(a_0 + \delta)) + t - (a_0 + \delta)$$

and the lemma follows.

Theorem :

With the assumptions of lemmas I and 2,

if further, $\int_0^U \frac{dt}{r(t)}$ is divergent for $U > 0$, then

point $x' = f(t, x)$ has at most one solution in the domain Δ through any point (a, b) .

Proof :

Suppose there exist two solutions say

$$\phi(t) \text{ and } \psi(t) \text{ with } \phi(a) = \psi(a) = b.$$

That is to say there exist points \tilde{a} (eg. $\tilde{a} \geq a$) where $\phi(\tilde{a}) \neq \psi(\tilde{a})$. Let the lower bound of those points \tilde{a} be a_0 . We have then $a_0 \leq a$ and $\phi(a_0) = \psi(a_0)$ but $\phi(t) \neq \psi(t)$ for $a_0 < t \leq a_0 + c$, where c is a certain positive number.

By virtue of our hypothesis we have

$$\begin{aligned} U(t) = |\phi(t) - \psi(t)| &\leq \int_{a_0}^t |f(s, \phi(s)) - f(s, \psi(s))| ds \\ &\leq \int_{a_0}^t V(s, U(s)) ds = P(t) > 0 \\ &\text{for } t > a_0 \end{aligned}$$

Using the Lemma 2 we have

$$M(P(t)) \leq M(P(a_0 + \delta)) + t - (a_0 + \delta) \quad \dots \quad (4)$$

with $\delta > 0$ and $a_0 + \delta < t$

$\delta \rightarrow 0+$, then

as

$$\begin{aligned} P(a_0 + \delta) \rightarrow 0, \quad M(P(a_0 + \delta)) &\rightarrow \int_{u_0}^0 \frac{dt}{r(t)} = -\infty \\ &\quad (u_0 > 0) \end{aligned}$$

But $M(P(t))$ is a finite number for $t > a_0$ i.e., (4) leads to a contradiction. We obtain the same contradiction for $t < a$. Therefore $\phi(t) \equiv \psi(t)$ in some

neighbourhood of a and by continuation of the solutions, it is also true in their whole interval of existence.

Cor : If $\int_0^u \frac{dt}{r(t)}$ is convergent for $u > 0$, then

we get from (4) for $\delta \rightarrow 0 +$

$$M(P(t)) \leq M(0) + t - a_0$$

Assuming $u_0 = 0$, it gives $M(0) = 0$ and

$$M(P(t)) \leq (t - a_0)$$

Therefore we have

$$U(t) \leq P(t) \leq M^{-1}(t - a_0) \quad t \geq a_0$$

where $M^{-1}(x)$ is inverse of $M(x)$.

That is if the solutions are not Unique, the difference of two solutions is subjected to the above estimation.

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STUDY OF COLOUR AND CONSTITUTION OF THE DYES OBTAINED FROM SUCCINIC ACID AND SUBSTITUTED SUCCINIC ACIDS

PART V. COLOUR AND CONSTITUTION

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[Received on 28th October, 1961]

ABSTRACTS

Four acids viz., phenylsuccinic, *o*-nitrophenylsuccinic, *p*-nitrophenylsuccinic and *o*-chlorophenylsuccinic acids were synthesised and condensed with phenol, resorcinol, phloroglucinol, pyrogallol, catechol and quinol. Thus, different succineins analogous to phthaleins were obtained. The absorption maxima of these succineins and of the phthaleins were observed to make a comparative study of the effect, if any, on light absorption of succinein dyes when drastic changes were made in the lower portion of phthaleins. The structural changes made in the lower portion of these dyes were of three kinds :

1. The benzenoid phthalic anhydride system was completely replaced by an aliphatic anhydride (succinic) system. This change does away with any possibility of conjugation of the central carbon atom with the lower portion.

2. One of the hydrogen atoms of one of the two -CH₂ groups of succinic acid was replaced by a phenyl group, thereby the conjugation of the central carbon atom is insulated.

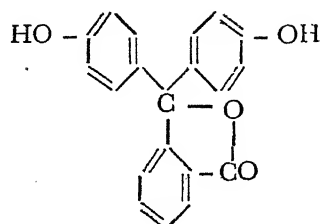
3. The introduced phenyl group was substituted by -NO₂ group in the ortho and para positions and with chlorine in the ortho position. These substitutions affected the distance between the two -COOH groups of the acids, which results in decrement of the yield of the dyes obtained.

A comparative study of these dyes with phthaleins showed that by changing the benzenoid system by a purely aliphatic and aryl substituted aliphatic systems and consequent removal of aromatic conjugation, the compounds begin to absorb at shorter wavelengths and the difference of absorption maxima λ_{\max} between the two series of dyes varies from 150 Å to 200 Å. Though the changes which are made, do not affect the charge that migrates between two aromatic nuclei in the upper portion of the molecule, yet as the number of π -electrons is decreased by removing the conjugation, the mobility or charge shifts may be reduced which may cause the molecule to absorb at higher frequencies.

We have already described in the previous papers our experimental work relating to the different series of succinein dyes which we have prepared (1,2,3,4). We shall discuss here the colour of these dyes with respect to their constitution.

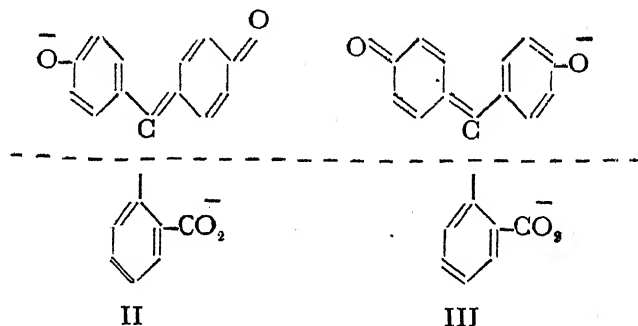
According to Lewis (5) if the colour of a compound is associated with an oscillation of positive charge along a given path, the frequency of absorption is increased by any change that diminishes the amount of positive charge and decreased by any change that increases it. In the same way where the colour is associated with an oscillation of negative charge, the absorption frequencies will be displaced accordingly towards higher or lower frequencies as the increase or decrease of the negative charge takes place.

In a neutral solvent, phenolphthalein has been shown to have the following lactone structure :



I

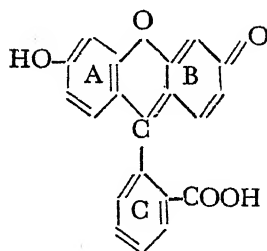
But in slightly alkaline medium it is turned red and this red colour is believed to be due to the presence of a divalent anion which is a hybrid of the two main resonating forms II and III:



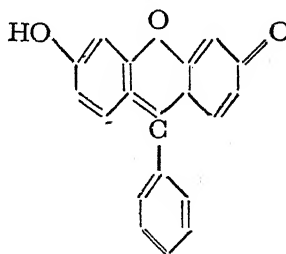
II

III

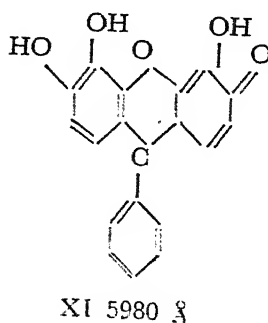
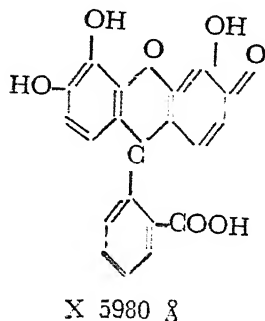
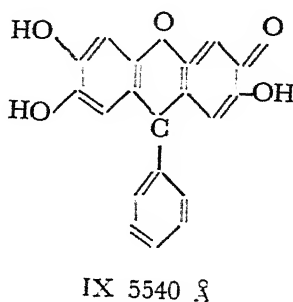
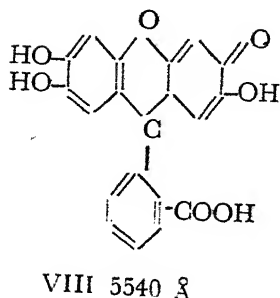
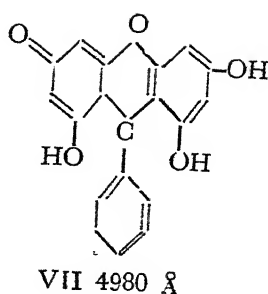
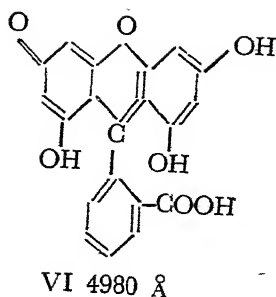
In the case of phthalein dyes, the charge oscillation takes place between the two terminal oxygen atoms as indicated in the structures II and III. In these the central carbon atom cannot take part in charge migration or charge resonance with all the three benzene nuclei. The part below the dotted line (in II and III) does not seem to take any active part in light absorption. As shown below, even the removal of carboxyl group in the following compounds (IV to XI) seems to make no difference in the wavelength of maximum absorption.



IV 4940 Å



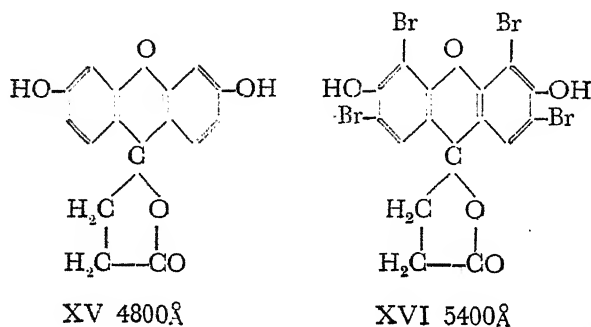
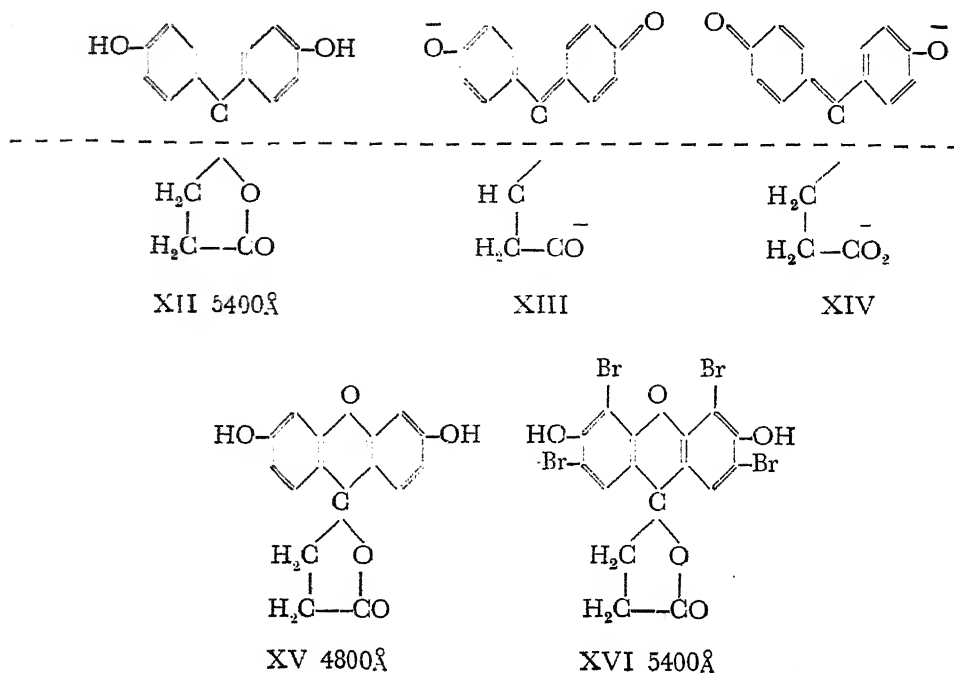
V 4940 Å



Here in all these compounds, the central carbon atom apparently cannot form double bonds with the ring C, hence it cannot take part in resonance with the ring C as it takes part in resonance with the other two rings, A and B, between which the charge migration takes place.

Since in phthaleins the terminal groups carry a negative charge, the absorption of light by these dyes will be shifted to lower frequencies by any change in structure which increases the acidity of the terminal group and vice-versa. Fluorescein differs from phenolphthalein only in the fact that the two rings between which the charge migration takes place are joined by an oxygen atom and thus a third ring is formed. Therefore, the charge that resonates between the two end oxygen atoms will be shared by the intermediate oxygen atom also in the case of fluorescein as a result of which the charge will decrease. Hence, fluorescein will absorb at higher frequencies as compared to phenolphthalein, and that is what we actually find. Similarly, eosin in which the acidity of the terminal oxygen atom is increased by the bromine substituent, absorbs at lower frequencies.

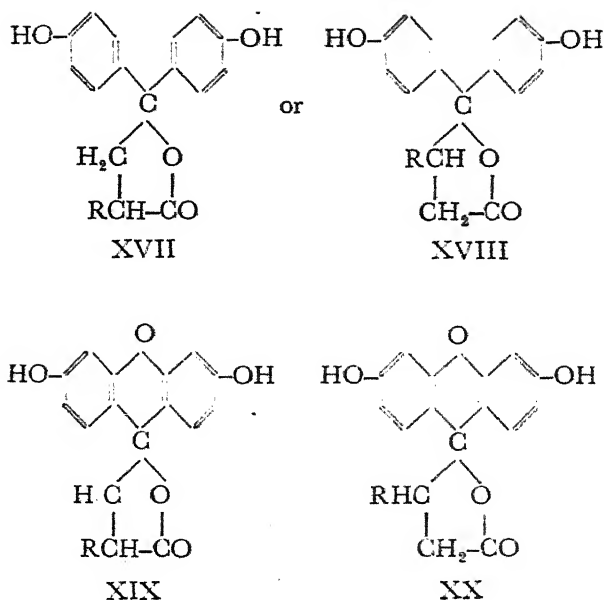
In succineins, the phthalic anhydride system has been replaced by succinic anhydride and aryl substituted succinic anhydride system. Thus, below the dotted line in XII to XIV is an aliphatic system instead of a benzenoid system.



Phenolsuccinein (XII) has maximum absorption at 5400 Å and resorcinolsuccinein (succinylfluorescein (XV) where the two rings have been joined together by an oxygen atom absorbs at 4800 Å. The tetrabromo derivative of succinylfluorescein (succinyl eosin, XVI) which is quite analogous to eosin, has the maximum absorption at 5400Å. The factors responsible for these differences in the absorption maxima of XII, XV and XVI are the same as discussed in the case of phthalein dyes proper.

Replacement of phthalic anhydride system by succinic anhydride system, removes the conjugation of the central carbon atom. As has already been stated, the colour of the phthaleins vary with the increase or decrease of the vibrating electric charges in the part of the molecule responsible for the colour above the dotted line, and also that any change in phthalic acid nucleus, *i.e.*, in the part below the dotted line produces no perceptible change.

In order to further elucidate effects, if any, produced by replacing the benzene nucleus below the dotted line in XII by an aliphatic and substituted aliphatic acid nucleus, study has been made of the compounds obtained from succinic acid and substituted succinic acids. The hydrogen atom in succinic acid was replaced by (i) C₆H₅ - ; (ii) C₆H₄NO₂ - (ortho); (iii) C₆H₄NO₂ - (para); and (iv) C₆H₄Cl - (ortho) and compounds analogous to phthaleins were obtained by condensing these with aromatic hydroxy compounds. The compounds prepared may have the following structures :



Where R = H, Succinic acid

= C₆H₅ -, Phenylsuccinic acid

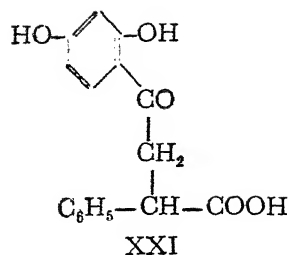
= C₆H₄NO₂ (ortho), *o*-Nitrophenylsuccinic acid

= C₆H₄NO₂ (para), *p*-Nitrophenylsuccinic acid

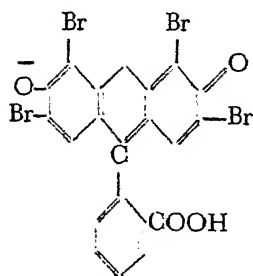
= C₆H₄ Cl (ortho), *o*-Chlorophenylsuccinic acid

From the above structures it appears that condensation of the aromatic hydroxy compounds may take place at either of the two >C=O groups. Steric considerations imply that condensation will take place not at the >C=O group adjacent to phenyl substituted carbon atom, but at the group situated further off from it. It is possible that both the compounds may be formed during the reaction but in quite different proportion. No doubt, during condensation two different compounds are produced but not in equal quantities. The compounds XVII and XIX are the main products with a little of XVIII and XX which could not be isolated in sufficient quantities. The caustic potash fusion of the compound XIV was repeated several times under different experimental conditions but it did not give any satisfactory result. It was found difficult to disintegrate the dye molecule and whatever little disintegration took place, the compound obtained was very little in quantity. It was not sufficient for studying it in detail.

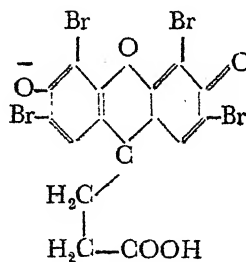
The product obtained by caustic potash fusion was almost colourless, the quantity obtained, as has been cited before, was very little. On steric consideration it can be given the following tentative structure XXI. The acid may be called α -phenyl- β -dihydroxybenzoyl propionic acid. Further studies in this connection are in progress.



On making a comparative study of the absorption maxima of phenolphthalein, fluorescein and eosin with those of corresponding succinic acid compounds, it appears that by the replacement of aromatic nucleus by an aliphatic nucleus and consequent removal of conjugation, the compounds begin to absorb at shorter wavelengths. Absorption of phenolphthalein with a little of alkali is 5600 Å (as obtained by the apparatus) and that of corresponding phenolsuccinein is 5400 Å, a difference of 200 Å, and that of fluorescein is at 5400 Å (as obtained with the apparatus), while that of the corresponding succinylfluorescein is at 4800 Å which ought to be the case as the number of π electrons decreased. In the case of eosin (XXII) the absorption maximum is less. It is at 5250 Å. While that of the corresponding succinic acid compound (XXIV) is at 5400 Å (as obtained from the apparatus). It is because as is apparent from the structural formulae given below (XXII and XXIII), the charge on bromine atom is lessened, while in the case of succinic acid compound it is stationary.



(XXII) 5250 Å



(XXIII) 5400 Å

Now, considering the case of phenylsuccinic acid compounds, the conjugation of the aromatic nucleus and the central carbon atom is separated by a $-\text{CH}_2$ group, i.e., the conjugation is insulated. The hydrolysis constant values also show that the two $-\text{COOH}$ groups are brought nearer together, i.e., the formation of anhydride is facilitated and the anhydride ring becomes more stabilised. Hence, only the yield of the dye-stuff will be increased and there will be no great change in absorption maxima. This is borne out by the data obtained.

In the case of ortho- and para-nitrophenyl substituted acids the values for K_1 are nearly the same as in succinic acid but the values for K_2 are much less, which connotes that the anhydride formation will not be easier and consequently the yield of the dye-stuff will be decreased which is actually the case and there is little possibility of the compounds behaving differently from succinic acid compounds as $-\text{NO}_2$ group in ortho position does not activate the ortho position and same will be the case with *p*-Nitrophenylsuccinic compounds.

In *o*-chlorophenylsuccinic acid compounds there is decrease in K_2 value and also a little decrease in K_1 value as compared to succinic acid. This also indicates that the two carboxyl groups are here more distant than in succinic acid, which fact will affect only the yield of the compound and not the absorption maxima. From these data it appears that the change in K_1 and K_2 does not materially affect the absorption maxima of the compounds i.e., the increase or decrease in the charges in the lower portion does not materially affect the colouring property of the compounds.

The slight variation, however, observed in few cases in the wavelength of maximum absorption, cannot be accounted for, unless and until correct correlation between electronic oscillation and atomic vibration is stabilised. From the nature of the compounds studied, it is obvious that though there are drastic changes in the lower part, as is evident from the hydrolysis constant (K_1 and K_2) of the acids given below from which succineins were prepared, no change in the charge migration in the upper portion of the molecule is observed as there is no change in the value of wavelength of maximum absorption.

Acids	Hydrolysis constants at 30°C
1. Succinic Acid	... $K_1 = 6.607 \times 10^{-5}$ $K_2 = 2.291 \times 10^{-6}$
2. Phenylsuccinic Acid	... $K_1 = 2.089 \times 10^{-4}$ $K_2 = 5.495 \times 10^{-6}$
3. <i>o</i> -Nitrophenylsuccinic Acid	... $K_1 = 6.31 \times 10^{-5}$ $K_2 = 1.995 \times 10^{-12}$
4. <i>p</i> -Nitrophenylsuccinic Acid	... $K_1 = 6.331 \times 10^{-5}$ $K_2 = 1.995 \times 10^{-12}$
5. <i>o</i> -Chlorophenylsuccinic Acid	... $K_1 = 1.26 \times 10^{-5}$ $K_2 = 1.413 \times 10^{-12}$

The absorption maxima were obtained with a Unicam Spectrophotometer.

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ON GENERALISED LAPLACE TRANSFORMS AND INFINITE INTEGRALS INVOLVING G- AND E- FUNCTIONS

By

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[Received on 4th November, 1961]

1. *Introduction* :—In some of his previous papers (10, 11) the author has evaluated some Infinite Integrals involving Meijer's G- Function. Here, with the aid of two theorems on Generalised Laplace Transforms some more integrals involving G- Function and the E- Function of MacRobert have been obtained.

The results derived are believed to be new.

Meijer (1941) gave a generalisation of the classical Laplace Transform

$$f(p) = p \int_0^{\infty} e^{-px} h(x) dx, \quad R(p) > 0 \quad \dots (1.1)$$

in the form

$$\phi(p) = p \int_0^{\infty} e^{-\frac{1}{2}px} (px)^{-k-\frac{1}{2}} W_{k+\frac{1}{2},m}(px) h(x) dx, \quad \dots (1.2)$$

$$R(p) > 0$$

while Varma (1951) gave the form

$$\psi(p) = p \int_0^{\infty} e^{-\frac{1}{2}px} (px)^{m-\frac{1}{2}} W_{k,m}(px) h(x) dx, \quad \dots (1.3)$$

$$R(p) > 0$$

Denoting (1.1) symbolically as usual by

$$f(p) \doteq h(x)$$

we shall represent (1.2) and (1.3) as

$$\phi(p) \frac{M}{k,m} h(x)$$

$$\text{and } \psi(p) \frac{V}{k,m} h(x) \quad , \text{ which reduced to (1.1) when } k = \pm m \text{ and}$$

$k + m = \frac{1}{2}$ respectively.

2. Theorem 1 :—

$$\text{If } \psi(p) = \frac{M}{k, m} x^{l-2} h(x)$$

$$h(p) \doteq x^{l-2k-3} \phi(x)$$

and

$$\phi(p) \doteq f(x)$$

then

$$\psi(p) = 2^{-2k-1} \int_0^\infty G_{2,3}^{3,1} \left(x^{2k-l+1, 0} \right. \\ \left. -1, k+m, k-m \right) x f\left(\frac{x}{p}\right) dx \quad \dots (2.1)$$

provided $R(p) > 0$, $R(l-k \pm m) > 0$ and the integral involved is convergent.

Proof :— Putting

$$\phi(z) = z \int_0^\infty e^{-zy} f(y) dy$$

in

$$h(x) = x \int_0^\infty e^{-xz} z^{l-2k-3} \phi(z) dz$$

and interchanging the order of integration, we obtain

$$h(x) = x \Gamma(l-2k-1) \int_0^\infty (x+y)^{2k-l+1} f(y) dy$$

Substituting this in equation (1.2), again interchanging the order of integration and using equation (32) on page 237 of (3) viz.,

$$\int_0^\infty (x+y)^{-\rho} x^\lambda e^{-\frac{1}{2}ax} W_{k,\mu}(ax) dx = \frac{y^{\lambda+1-\rho}}{\Gamma(\rho)} G_{2,3}^{3,1} \left(ay \right. \\ \left. -\lambda, 1-k \right. \\ \left. \rho-\lambda-1, \frac{1}{2}+\mu, \frac{1}{2}-\mu \right)$$

$$R(\lambda) > |R(\mu)| - \frac{3}{2}, R(a) > 0$$

we obtain the theorem.

Example :— Taking

$$f(x) = 2^{-2\nu - \frac{1}{2}} x^{-\nu + \frac{1}{4}} (1+x)^{-\frac{1}{2}} P_{2\mu - \frac{1}{2}}^{2\nu + \frac{1}{2}}(1+x)^{\frac{1}{2}}$$

we have (2), page 294,

$$\phi(p) = p^{\nu + \frac{1}{2}} e^{\frac{1}{2}p} W_{\nu, \mu}(p); \quad \nu < \frac{1}{4}$$

Then, finding the Laplace Transform of $x^{l-2k-3} \phi(x)$ (2, p. 216), we get

$$h(p) = \frac{\Gamma(l-2k+\nu \pm \mu - 1)}{\Gamma(l-2k-\frac{1}{2})} p^{2k-l-\nu-\mu+2} {}_2F_1 \left[\begin{matrix} \mu & l-2k+\nu-1, \mu-\nu+\frac{1}{2} \\ l-2k-\frac{1}{2} \end{matrix}; 1 - \frac{1}{p} \right]$$

where $R(p) > 0$, $R(l-2k-\nu \pm \mu - 1) > 0$.

To obtain the Meijer Transform of $x^{l-2} h(x)$ we use the result (11, p. 172)

$$x^{k+l+\delta-\frac{1}{2}} {}_2F_1 \left[\begin{matrix} a, b \\ c \end{matrix}; 1 - \frac{1}{x} \right] \frac{M}{k, m} \frac{p^{-l-k-\frac{1}{2}} \Gamma(c)}{\Gamma(a) \Gamma(c-a) \Gamma(c-b) \Gamma(b)} \\ \times G_{3,4}^{4,2} \left(p \left| \begin{matrix} 1-\delta-a, 1-\delta-b, l-k+\frac{1}{2} \\ -\delta, c-a-b-\delta, l+m+\frac{1}{2}, l-m+\frac{1}{2} \end{matrix} \right. \right)$$

where $R(p) > 0$, $R(l \pm m + a + \delta + \frac{1}{2}) > 0$, $R(c-a-b) > 0$,

$R(l \pm m + b + \delta + \frac{1}{2}) > 0$

Substituting in the theorem, we get after a little simplification and putting

$$k = \frac{1}{2}(b+c), m = \frac{1}{2}(b-c), l = b+c-a+1, \nu = \rho - 1/4$$

$$\int_0^\infty x^{1-\rho}(p+x)^{-\frac{1}{2}} G_{2,3}^{3,1} \left(x \left| \begin{matrix} a, 0 \\ -1, b, c \end{matrix} \right. \right) E_{2\mu-\frac{1}{2}}^{2\rho} \left(1 + \frac{x}{p} \right)^{\frac{1}{2}} dx \\ = \frac{2^{2\rho} p^{a-\rho-1-\frac{1}{2}(b+c)}}{\Gamma(3/4-\rho \pm \mu)} G_{3,4}^{4,2} \left(p \left| \begin{matrix} \frac{1}{2}(b+c) + \frac{3}{2}, \frac{1}{2}(b-c) - a + 2\rho + \frac{1}{2}, \frac{1}{2}(b+c) - a + \frac{3}{2} \\ \frac{1}{2}(b+c) - a + \rho + 1/4 \pm \mu, \frac{3b-c}{2} - a + \frac{3}{2}, \frac{b}{2} + \frac{3c}{2} - a + \frac{3}{2} \end{matrix} \right. \right)$$

where $R(p) > 0$, $R(b-a+1) > 0$, $R(c-a+1) > 0$, $R(c-a-b) > 0$

$R(b-2\rho+2) > 0$, $R(c-2\rho+2) > 0$ and $\rho < \frac{1}{2}$... (2.2)

3. Theorem : 2.

If $\psi(p) \doteq x^{-\gamma} g(x)$

$$g(p) \frac{V}{\sigma, \mu} x^{2-2\gamma} \phi\left(\frac{1}{x}\right)$$

and

$$\phi(p) \frac{V}{k, m} f(x),$$

then

$$\psi(p) = p \int_0^{\infty} x^{-\gamma} E \left[\begin{matrix} 2-\gamma, \gamma, \gamma+2m \\ \frac{5}{2} + \mu - \gamma - \sigma \end{matrix} ; \frac{x}{p} \right] f(x) dx \quad \dots (3.1)$$

where $\gamma = \frac{3}{4} + \mu - \frac{m}{2} + \frac{k}{2}$, the integral being convergent and

$$R(\gamma) > 0, R(2 - \gamma) > 0, R(\gamma + 2m) > 0, R(2 - \gamma + 2\mu) > 0$$

Proof:—The Parseval-Goldstein Theorem of the Laplace Transform (4) may be generalised in case of Varma Transform and may be stated thus :

$$\text{If} \quad \phi_1(p) \frac{V}{k, m} f_1(x)$$

$$\text{and} \quad \phi_2(p) \frac{V}{k, m} f_2'(x)$$

then provided the integrals converge

$$\int_0^{\infty} f_1(t) \phi_2(t) \frac{dt}{t} = \int_0^{\infty} f_2(t) \phi_1(t) \frac{dt}{t} \quad (A)$$

Now, Rathie (6) p. 383 has shown that

$$e^{-ax} x^{\alpha-1} \frac{V}{\sigma, \mu} \frac{\Gamma(\alpha) \Gamma(\alpha + 2\mu)}{\Gamma(\alpha + \mu - \sigma + \frac{1}{2})} p^{1-\alpha} {}_2F_1 \left[\begin{matrix} \alpha, \alpha + 2\mu \\ \alpha + \mu - \sigma + \frac{1}{2} \end{matrix} ; \frac{a}{p} \right]$$

$$R(\alpha) > 0, R(\alpha + 2\mu) > 0, R(a) > 0, R(p) > 0.$$

Taking this with the relation

$$g(p) \frac{V}{\sigma, \mu} x^{2-2\gamma} \phi\left(\frac{1}{x}\right)$$

we obtain, with the use of theorem (A), on putting $\alpha = 2 - \gamma$,

$$\frac{\Gamma(\frac{5}{2} + \mu - \sigma - \gamma)}{\Gamma(2 - \gamma) \Gamma(2 - \gamma + 2\mu)} \int_0^{\infty} x^{-\gamma} e^{-ax} g(x) dx = \int_0^{\infty} x^{\gamma-2} {}_2F_1 \left[\begin{matrix} 2 - \gamma, 2 - \gamma + 2\mu \\ \frac{5}{2} + \mu - \sigma - \gamma \end{matrix} ; -ax \right] \phi(x) dx \quad \dots (3.2)$$

Again taking the pairs (6, p. 384)

$$(ax)^{\gamma-1} {}_2F_1 \left[\begin{matrix} \beta, \gamma + m - k + \frac{1}{2} \\ \delta \end{matrix} ; -ax \right] \frac{V}{k, m} \frac{\Gamma(\delta) (p/a)^{1-\gamma}}{\Gamma(\beta) \Gamma(\gamma + m - k + \frac{1}{2})} \\ \times E \left[\begin{matrix} \beta, \gamma, \gamma + 2m \\ \delta \end{matrix} ; \frac{p}{a} \right]$$

and

$$\phi(p) \frac{V}{k, m} f(x).$$

we obtain on using (A)

$$\int_0^\infty x^{\gamma-2} {}_2F_1 \left[\begin{matrix} \beta, \gamma + m - k + \frac{1}{2} \\ \delta \end{matrix} ; -ax \right] \phi(x) dx \quad \dots (3.3) \\ = \frac{\Gamma(\delta)}{\Gamma(\beta) \Gamma(\gamma + m - k + \frac{1}{2})} \int_0^\infty x^{-\gamma} E \left[\begin{matrix} \beta, \gamma, \gamma + 2m \\ \delta \end{matrix} ; \frac{x}{a} \right] f(x) dx$$

Now, putting $\gamma = \frac{1}{2} + \mu - \frac{m}{2} + \frac{k}{2}$, $\delta = \frac{1}{2} - \gamma + \mu - \sigma$

and $\beta = 2 - \gamma$

and replacing a by p we obtain, in virtue of (3.2) and (3.3) and

$$\psi(p) \doteq x^{-\gamma} g(x),$$

the theorem under the conditions stated.

Corollary :— If we take $\sigma = -\mu + \frac{1}{2}$

and $k = -m + \frac{1}{2}$

the theorem reduces to

$$\text{If } \psi(p) \doteq x^{m-\mu-1} g(x),$$

$$g(p) \doteq x^{2m-2\mu} \phi\left(\frac{1}{x}\right)$$

and

$$\phi(p) \doteq f(x),$$

then

$$\psi(p) = p \int_0^{\infty} x^{m-\mu-1} E\left[1+\mu-m, 1+\mu+m; \frac{x}{p}\right] f(x) dx \quad \dots(3.4)$$

where $R(1+\mu \pm m) > 0$ and the integral involved is convergent.

Example 1: Taking

$$f(x) = x^{-\lambda-\mu-2m-\frac{1}{2}} {}_2F_1\left[\begin{matrix} \frac{1}{2}-\lambda+\mu, 1-\lambda-\mu-k-m \\ \frac{1}{2}-\lambda-\mu-2m \end{matrix}; -x\right]$$

we have (6, p. 283)

$$\phi(p) = \frac{\Gamma(\frac{1}{2}-\lambda-\mu) \Gamma(\frac{1}{2}-\lambda-\mu-2m)}{\Gamma(1-\lambda-\mu-m-k)} p^{2m+\mu+\frac{1}{2}} e^{\frac{1}{2}p} W_{\lambda, \mu}(p)$$

$$R(\frac{1}{2}-\lambda-\mu) > 0, R(\frac{1}{2}-\lambda-\mu-2m) > 0,$$

so that (8, p. 273)

$$g(p) = \frac{\Gamma(\frac{1}{2}-\lambda-\mu-2m) \cdot p}{\Gamma(\frac{1}{2}-\lambda+\mu) \Gamma(1-\lambda-\mu-k-m)} G_{2,4}^{4,1}\left(p \left| \begin{matrix} \lambda+m+k+3\mu, \frac{1}{2}-\sigma+\mu \\ 2\mu, 0, m+k+3\mu \pm \mu - \frac{1}{2} \end{matrix} \right. \right)$$

$$\text{where } R(p) > 0, R(\lambda-m-k-2\mu \pm \mu+1) > 0$$

Finding $g(x)$ and using (2, p. 222)

$$i^{-\sigma} G_{h,k}^{l,n}\left(i \left| \begin{matrix} \alpha_1 \dots \alpha_h \\ \beta_1 \dots \beta_k \end{matrix} \right. \right) \doteq p^{\sigma} G_{h+1,k}^{l,n+1}\left(\sigma, \alpha_1 \dots \alpha_h \right| \beta_1 \dots \beta_k)$$

$$(h+k) < 2(l+n),$$

$$R(\sigma-1) < R(\beta_j) \text{ if } h < k \text{ and } R(p) > 0 \Big| \text{ if } h=k \text{ and } R(p) > 1 \Big| j = 1, \dots, l$$

$$|\arg p| < (l+n-\frac{1}{2}h-\frac{1}{2}k)\pi$$

we obtain

$$\psi(p) = \frac{\Gamma(\frac{1}{2}-\lambda-\mu-2m) \cdot p^{\mu-\frac{m}{2}+\frac{k}{2}-1/4}}{\Gamma(\frac{1}{2}-\lambda+\mu) \Gamma(1-\lambda-\mu-k-m)} \times G_{3,4}^{4,2}\left(\frac{1}{p} \left| \begin{matrix} \gamma-1, \lambda+m+k+3\mu, \frac{1}{2}-\sigma+\mu \\ 2\mu, 0, m+k+3\mu \pm \mu - \frac{1}{2} \end{matrix} \right. \right)$$

$$\text{Putting } (\frac{1}{2}-\lambda+\mu) = a, (1-\lambda-\mu-k-m) = b, (\frac{1}{2}-\lambda-\mu-2m) = c \\ \text{and } \frac{5}{2}+\mu-\sigma-\gamma = \delta$$

we have ultimately

$$\int_0^{\infty} x^{c-\gamma-1} E \left[\begin{matrix} 2-\gamma, \gamma, a-b-\gamma+2 \\ \delta \end{matrix} ; \frac{x}{p} \right] {}_2F_1 \left[\begin{matrix} a, b \\ c \end{matrix} ; -x \right] dx$$

$$= \frac{\Gamma(c) p^{\gamma-2}}{\Gamma(a) \Gamma(b)} G_{3,4}^{4,2} \left(\frac{1}{p} \middle| \begin{matrix} \gamma-1, 2\gamma-c-1, \gamma+\delta-2 \\ b-c+2\gamma-2, 0, a-c+2\gamma-2, a-b \end{matrix} \right)$$

where $R(2-\gamma) > 0, R(\gamma) > 0, R(a-b-\gamma+2) > 0, R(b-c+\gamma) > 0, R(c) > 0$ (3.5)
 $R(a-b+c-2\gamma+2) > 0, R(2b-2a-c+2\gamma-1) > 0.$

Example 2: Taking

$$\text{where } f(x) = x^{\nu} X_{\nu, k, m}^{*}(n)$$

$$X_{\nu, k, m}(x) = \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \sum_{r=0}^{\infty} \frac{(\frac{1}{2}-m-k)_r \Gamma(\nu+\frac{3}{2}+m-k+r)}{(1-2m)_r \Gamma^{*}(\nu+1+m \pm m+r)} \cdot \frac{x}{r!}$$

$$\times {}_1F_2 \left[\begin{matrix} \nu+\frac{3}{2}+m-k+r \\ \nu+m+1 \pm m+r \end{matrix} ; -x \right]$$

$$+ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \sum_{r=0}^{\infty} \frac{(\frac{1}{2}+m-k)_r \Gamma(\nu+\frac{3}{2}+3m-k+r)}{(1+2m)_r \Gamma^{*}(\nu+1+3m \pm m+r)} \cdot \frac{x^{2m+r}}{\gamma!}$$

$$\times {}_1F_2 \left[\begin{matrix} \nu+\frac{3}{2}+3m-k+r \\ \nu+1+3m \pm m+r \end{matrix} ; -x \right]$$

so that (7, p. 274)

$$\phi(p) = p^{-\nu-m+\frac{1}{2}} e^{-\frac{1}{2}p} W_{k, m} \left(\frac{1}{p} \right)$$

where $R(p) > 0, R(\nu+1+2m \pm 2m) > 0$ and $2m$ is not an integer or zero, giving

$$x^{2-2\gamma} \phi \left(\frac{1}{x} \right) = x^{\frac{3}{2}-2\gamma+\nu+m} e^{-\frac{1}{2}x} W_{k, m}(x),$$

*Defined by Roopnarain (7, p. 270)

$$X_{\nu, k, m}(x) = O(x^{m \pm n}) \text{ for small } x$$

$$\sim x^{-\lambda} \quad \text{where } \lambda = \frac{1}{2}(\nu + \frac{1}{2}), \frac{1}{2} + k - m;$$

$$\Gamma^{*}(a \pm b) \text{ is used to denote } \Gamma(a+b) \Gamma(a-b)$$

and ${}_pF_q \left[\begin{matrix} \alpha_1 \pm \beta_1, \alpha_2 \pm \beta_2, \dots \\ \gamma_1 \pm \delta_1, \gamma_2 \pm \delta_2, \dots \end{matrix} ; x \right]$ to denote ${}_pF_q \left[\begin{matrix} \alpha_1 + \beta_1, \alpha_1 - \beta_1, \alpha_2 + \beta_2, \alpha_2 - \beta_2, \dots \\ \gamma_1 + \delta_1, \gamma_1 - \delta_1, \gamma_2 + \delta_2, \gamma_2 - \delta_2, \dots \end{matrix} ; x \right]$

we get (8, p. 273)

$$g(p) = G_{3,3}^{2,2} \left(\frac{1}{p} \left| \begin{matrix} 0, -2\mu, \frac{3}{2} - k - 2\gamma + \nu + m \\ 2 - 2\gamma + \nu + 2m, 2 - 2\gamma + \nu, \sigma - \mu - \frac{1}{2} \end{matrix} \right. \right)$$

where $R(3 - 2\gamma + \nu + m \pm m + \mu \pm \mu) > 0$

Finding $x^{-\gamma} g(x)$ and using (1, p. (209)

$$G_{p,q}^{m,n} \left(\frac{1}{x} \left| \begin{matrix} \alpha_r \\ \beta_s \end{matrix} \right. \right) = G_{q,p}^{n,m} \left(x \left| \begin{matrix} 1 - \beta_s \\ 1 - \alpha_r \end{matrix} \right. \right)$$

we get

$$\psi(p) = p^\gamma G_{4,3}^{2,3} \left(\frac{1}{p} \left| \begin{matrix} \gamma, 2\gamma - 2m - \nu - 1, 2\gamma - \nu - 1, \frac{3}{2} - \sigma + \mu \\ 1, 1 + 2\mu, 2\gamma - k - \nu - m - \frac{3}{2} \end{matrix} \right. \right)$$

Expressing $\chi_{\nu, k, m}(x)$ in terms of G-Function (6, p. 271)

$$\chi_{\nu, k, m}(x) = x^{-\nu} G_{2,4}^{2,1} \left(x \left| \begin{matrix} k - m - \frac{1}{2}, \nu - k + m + \frac{1}{2} \\ \nu, \nu + 2m, -2m, 0 \end{matrix} \right. \right)$$

we may write the result thus :—

$$\begin{aligned} & \int_0^\infty x^{-\gamma} E \left[\begin{matrix} 2 - \gamma, \gamma, \gamma + 2m \\ \frac{3}{2} - \gamma + \mu - \sigma \end{matrix} : \frac{x}{p} \right] G_{2,4}^{2,1} \left(x \left| \begin{matrix} k - m - \frac{1}{2}, \nu - k + m + \frac{1}{2} \\ \nu, \nu + 2m, -2m, 0 \end{matrix} \right. \right) dx \\ &= \int_0^\infty x^{\nu-\gamma} E \left[\begin{matrix} 2 - \gamma, \gamma, \gamma + 2m \\ \frac{3}{2} - \gamma + \mu - \sigma \end{matrix} : \frac{x}{p} \right] \chi_{\nu, k, m}(x) dx \\ &= p^{\gamma-1} G_{4,3}^{2,3} \left(\frac{1}{p} \left| \begin{matrix} \gamma, 2\gamma - \nu - 2m - 1, 2\gamma - \nu - 1, \frac{3}{2} - \sigma + \mu \\ 1, 1 + 2\mu, 2\gamma + k - \nu - m - \frac{3}{2} \end{matrix} \right. \right) \dots (3.6) \end{aligned}$$

where $\gamma = \frac{3}{4} + \mu - \frac{m}{2}, \frac{k}{2}, R(\gamma) > 0, R(2 - \gamma) > 0, R(p) > 1$

$R(3 - 2\gamma + \nu + m + \mu \pm m \pm \mu) > 0$ and $2m$ is not an integer or zero. Also $R(\gamma + 2m) > 0, R(2 - \gamma + 2\mu) > 0, R(\nu + 1 + 2m \pm 2m) > 0$.

I am greatly indebted to Dr. P. L. Srivastava for his valuable guidance.

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- | | |
|---|--|
| 1. Place of Publication | ... The National Academy of Sciences, India,
Lajpatrai Road, Allahabad-2 (U.P.) |
| 2. Periodicity of its publication | ... Quarterly. |
| 3. Printer's Name | ... M. Sarwat Husain. |
| Nationality | ... Indian. |
| Address | ... 170, Noorulla Road, Allahabad. |
| 4. Publisher's Name | ... Dr. R. K. Saksena. |
| Nationality | ... Indian. |
| Address | ... 1, B-Beli Road, Allahabad-2. |
| 5. Editor's Name | ... Dr. R. K. Saksena. |
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| 6. Names and addresses of individuals who own the newspaper and partners or shareholders holding more than one per cent of the total capital. | The National Academy of Sciences,
India, Lajpatrai Road, Allahabad-2
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Published by Dr. R. K. Saxena, for the National Academy of Sciences, India, Allahabad
and Printed by M. Sarwat Husain at The Mission Press, Allahabad

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